

MEASUREMENTS OF DIELECTRIC CONSTANTS AND ELECTRIC DIPOLE MOMENTS IN THE GAS PHASE

Kai Bergström

IR 7314

Dept. of Applied Electronics Thermochemistry Laboratory
Lund Institute of Technology Chemical Center
Lund, Sweden University of Lund

Lund 1973

MEASUREMENTS OF DIELECTRIC CONSTANTS AND ELECTRIC DIPOLE
MOMENTS IN THE GAS PHASE

AKADEMISK AVHANDLING

som för avläggande av filosofie doktorsexamen
vid matematisk-naturvetenskapliga fakulteten
vid universitetet i Lund kommer att offentligen
försvaras å Kemicentrum, hörsal G, fredagen
den 5 oktober 1973 kl. 1015

av

Kai Bergström
Fil. kand., Ld



MEASUREMENTS OF DIELECTRIC CONSTANTS AND ELECTRIC
DIPOLE MOMENTS IN THE GAS PHASE

Kai Bergström

IR 7314

Dept. of Applied Electronics
Lund Institute of Technology
Lund, Sweden

Thermochemistry Laboratory
Chemical Center
University of Lund

Lund 1973



Digitized by the Internet Archive
in 2026



SUMMARY.

A transformer bridge with capacitors suitable for low pressure gas phase measurements of dielectric constants has been developed. A relative capacitance resolution of two parts in 10^8 has been obtained. The dielectric constant (relative permittivity) of four non-polar gases has been determined: $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm} \cdot 10^6}$ is $516,69 \pm 0,4$ for argon, $922,18 \pm 0,3$ for carbon dioxide, $253,80 \pm 0,3$ for hydrogen, and $547,32 \pm 0,3$ for nitrogen. The electric dipole moment in the gas phase has been determined with the temperature variation method for three ketones: acetone, $2,87 \pm 0,01$ D, 2,2,4-trimethyl-3-pentanone, $2,86 \pm 0,06$ D and 2,2,4,4-tetramethyl-3-pentanone, $2,67 \pm 0,08$ D.

CONTENTS

	Page
1. GENERAL INTRODUCTION	1
1.1. History of dielectric theory.	1
1.2. Historic notes and principles of the atomic beam method.	4
1.3. Historic notes and principles of microwave spectroscopy.	5
1.4. Volume of work on dipole moment determinations.	7
2. GENERAL CONSIDERATIONS ON GAS PHASE DIPOLE MOMENT MEASURING METHODS	8
2.1. Molecular beam method.	8
2.2. Dielectric temperatures variation method.	8
2.3. Microwave spectroscopy.	9
2.4. Accuracy of dipole moments measured with different methods.	9
2.5. Limiting factors for different methods.	10
3. GAS PHASE MEASUREMENTS VERSUS MEASUREMENTS IN SOLUTIONS	12
4. GENERAL CONSIDERATIONS ON THE DIELECTRIC TEMPERATURE VARIATION METHOD FOR GAS PHASE MEASUREMENTS	13
4.1. Quantities to be measured in the Debye equation.	13
4.2. Frequency dependence of the dielectric constant.	13
4.3. Definition of the dielectric constant and permittivity.	14
4.4. Determination of the gas density.	15
4.5. Temperature range.	15
5. EXPERIMENTAL DIELECTRIC METHODS FOR GAS PHASE MEASUREMENTS	17
5.1. Resonant circuits.	17
5.2. Heterodyne beat method.	19
5.2.1. The principle of the method.	19
5.2.2. Evaluation of the dielectric constant.	20
5.2.3. Drawbacks of the method.	21
5.2.4. Accuracy of the method.	22
5.2.5. Application at microwave frequencies.	23

5.3. Resonance methods.	23
5.4. Bridge methods.	24
5.5. Transformer bridge.	25
5.5.1. Development of the transformer bridge.	25
5.5.2. Principles of the bridge.	26
5.5.3. Three-terminal capacitors.	31
6. CONSTRUCTION OF A SENSITIVE TRANSFORMER BRIDGE	34
6.1. General considerations.	34
6.2. The transformer.	35
6.3. Capacitance substitution technique.	35
6.4. Substitution capacitances.	36
6.4.1. Design considerations.	36
6.4.2. Construction details.	39
6.4.3. "Scaling down" capacitors.	42
6.4.4. Mounting.	42
6.4.5. Calibration.	43
6.5. Capacitance measuring cells.	44
6.5.1. General demands.	44
6.5.2. Choice of capacitor type.	44
6.5.3. Guard electrodes.	45
6.5.4. Construction details of the first constructed capacitors.	48
6.5.5. Disadvantages of the first capacitors.	48
6.5.6. Construction details of the second capacitors.	49
6.5.7. Losses in a glass dielectric.	53
6.5.8. Temperature control.	55
6.6. Generator.	55
6.7. Indicator.	56
6.7.1. Noise sources.	56
6.7.2. Noise level reduction.	58
6.7.3. Operating frequency compared with the frequency region of dielectric dispersion.	58

6.8. System considerations.	59
6.8.1. Phase detection technique.	60
6.8.2. Phase detection applied to the measuring system.	62
6.8.3. Complete block schematic.	63
6.8.4. Environmental noise level reduction.	64
7. PERFORMANCE OF THE CAPACITANCE MEASURING SYSTEM	67
7.1. General	67
7.1.1. Sensitivity.	67
7.1.2. Overall stability.	67
7.1.3. Effects of atmospheric pressure and humidity.	68
7.1.4. Effects of temperature variations.	68
7.2. Performance tests.	69
7.2.1. Purity of the test gases.	69
7.2.2. Experimental procedure.	70
7.2.3. Evaluation of results.	71
7.2.4. Dielectric constants of argon, carbon dioxide, hydro- gen and nitrogen.	73
7.2.5. Comparison of results.	75
7.3. Performance tests at elevated temperatures.	79
7.4. Gas density measurements.	81
7.5. Tests of ampoule technique.	82
7.5.1. Purity of acetone sample	82
7.5.2. Experimental technique.	83
7.5.3. Molar polarization of acetone.	83
7.5.4. Adsorption test.	85
7.5.5. Dipole moment of acetone.	85
7.5.6. Comparison of results.	88
8. DIPOLE MOMENTS OF KETONES IN THE GAS PHASE	90
8.1. Vapour pressures of 2,2,4 - trimethyl - 3 - pentanone and 2,2,4,4 - tetramethyl - 3 - pentanone.	90

8.2. Experimental procedure and dipole moment of 2,2,4-trimethyl-3-pentanone.	91
8.3. Experimental procedure and dipole moment of 2,2,4,4-tetramethyl-3-pentanone.	93
8.4. Comparison of results with benzene solution measurements	96
8.5. Correlation between dipole moment and C-C-C bond angle at the carbonyl group.	98
ACKNOWLEDGEMENTS	101
APPENDIX	102
REFERENCES	104

1. GENERAL INTRODUCTION

1.1. History of dielectric theory

In 1837 Faraday¹ pointed out that particles of matter come into a constrained condition when subjected to an electric field in which they acquire positive or negative points or parts.

Mosotti² and then Clausius³ were the first in 1850 and 1879 respectively to try to give a quantitative relation between the dielectric constant, ϵ , for a substance and its molar polarization, P_M . They assumed that the molecules in a dielectric were perfectly conducting spheres (with the radii r) surrounded by an isolating vacuum. Thus they deduced the following expression:

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi}{3} \alpha N \quad (1)$$

where M is the molecular weight of the dielectric, ρ its density, α the polarizability, and N Avogadro's number. This expression (1) is usually referred to as the Clausius - Mosotti relation.

It follows from electrostatic considerations that

$$\alpha = r^3 \quad (2)$$

Consequently the molar polarization is equal to the volume of one mole of the molecules. Hence the radius of an atom can be calculated in simple cases with fairly good agreement with values obtained by other methods.

The Clausius - Mosotti relation (1) includes only the contribution to the molar polarization from induced dipoles and a term due to permanent dipoles has to be added. So at this time it was not possible to explain the experimentally observed temperature dependence of the dielectric constant for many substances. Also the depiction of molecules as conducting spheres is not satisfactory.

The polarization of a nonpolar dielectric is independent of the temperature, for the reason that if the molecule is turned in the electric field by thermal collisions, the induced dipole moment in the molecule will immediately realign in the electric field direction. However, in the case of a polar substance, its molecules will also have a permanent dipole moment. These molecules will have a preferential alignment in the direction of the electric field. An increase in temperature will decrease this line up of the dipoles because of increasing impact of random thermal collisions. A term that accounts for this additional orientation polarization, P_0 , should consequently be added to the induced polarization and may be deduced from the average components of the permanent dipoles in the electric field direction as a function of the temperature. This was first done by Debye^{4,5,6} in the early 1910's and he derived the following equation

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (3)$$

where μ is the permanent dipole moment, k the Boltzmann constant, and T the absolute temperature. The induced polarization

$$P_D = \frac{4\pi}{3} N\alpha \quad (4)$$

is the sum of the electronic polarization, P_E and the atomic polarization, P_A ,

$$P_D = P_E + P_A = \frac{4\pi}{3} N\gamma_E + \frac{4\pi}{3} N\gamma_A \quad (5)$$

where γ_E and γ_A are the contributions to the polarizability, α , from the electronic and atomic displacements respectively. The electronic displacement is due to the fact that the electric field will tend to separate the normal mean positions of the electrons relative to the atomic nuclei. Distortions of atomic bonds and valence angles produce the atomic polarizability.

Debye made the assumption that the molecules are so far apart that the dipoles do not exert electrical forces on one another, so that they are distributed according to Langevin's law^{7,8}. Also, there must be no local electric field from molecular dipoles within a sphere with a radius that must be large compared with the molecular dimensions. This second assumption restricts the validity of Debye's equation to gases at atmospheric and lower pressures and possibly to dilute solutions of polar substances in non-polar solvents.

Onsager⁹ has calculated the local electric field in order to get a more general equation than Debye's. However, Onsager used another model than the classical one of Debye.

Applying the quantum theory to solve the average moment in an electric field, Van Vleck^{10,11,12} derived a general equation for all types of molecules in the gas phase. This equation, however, is practically identical with Debye's equation with the exception of a small correction term added to the permanent polarization. This correction term is in most cases experimentally indistinguishable from zero.

At least 20 other equations¹³ have been derived to calculate dipole moment data from dielectric constant measurements. Most of these equations apply, however, to liquids and solutions.

From measurements of the dielectric constant of a gas as a function of the temperature, the dipole moment may easily be calculated from the slope of a plot of the molar polarization versus the inverse of the absolute temperature according to Debye's equation (3).

Beside the classical approach of Debye for determining the dipole moment via dielectric measurements there are approximately 20 other methods for the determination of dipole moments. Many of these methods are quite special as e.g. velocity of sound and fluorescence methods and many of them have been adapted to liquids.

Two important spectroscopic methods for gas phase measurements of electric dipole moment should be mentioned in brief, namely molecular beam electric resonance and molecular rotational resonance.

1.2. Historic notes and principles of the atomic beam method

The first experiment with an atomic beam was the famous one of Gerlach and Stern¹⁴. They determined the magnetic moment of silver atoms. This technique was transferred to its electric analogy first by Estermann and Fraser¹⁵ in 1933. Rabi et.al.¹⁶ constructed, in 1938, a new molecular (or atomic) beam apparatus, which in addition to the two inhomogeneous magnetic fields, also contained a homogeneous magnetic field and a microwave field. This new technique greatly improved accuracy and sensitivity. In the electrical version molecules are injected into a vacuum chamber through a series of slits thus defining a narrow molecular ribbon or beam. The beam traverses an inhomogeneous, relatively weak, deflecting electric field and passes through another slit. The beam is eventually

focused on a detector by a second, stronger, inhomogeneous field with the direction of the field gradient reversed. The molecules hitting the detector will be in the same rotational state if the two fields and their inhomogeneity are properly adjusted. If a homogeneous electric field is placed between the two other fields and a microwave field is superimposed on the homogeneous field in parallel or perpendicular to it, this field or the microwave field can be adjusted to give a rotational resonance in the beam. This resonance is indicated as a null in the detector since the second inhomogeneous field no longer refocuses the molecules on the detector. From determinations of the homogeneous field and the microwave frequency the dipole moment of the molecule can be calculated.

1.3. Historic notes and principles of microwave spectroscopy

The other spectroscopic method, molecular rotational resonance, MRR, or microwave spectroscopy as it is usually called dates back in 1933 when Cleeton and Williams¹⁷ made a microwave spectrum of ammonia of 24 GHz.

Like other spectrometers, a microwave spectrometer contains a radiation source, a frequency measuring device, an absorption cell, and a detector. The radiation source was usually a klystron which has an electric detuning range of 100-200 Mhz, but today the klystron is often replaced by a BWO (backward wave oscillator) with a tuning range of many gigahertz. The frequency measuring device can be a simple wavemeter with an accuracy of a few megahertz or a complex frequency counting system locked to a frequency standard and with a readout in kilohertz or less. The sample cell in its most simple form is a length of waveguide or sometimes a stripline, which can be evacuated and to which a gas of low pressure (10^{-2} - 10^{-4} mmHg) can be admitted. The absorption cell almost exclusively used now is the Stark cell which is a length of waveguide with a metal septum suspended in the middle of the waveguide along its

length. The septum is insulated from the waveguide walls so that it is possible to apply a quite high voltage between the septum and the waveguide walls to produce a static electric field. The microwave power is detected by a microwave diode. If the microwave frequency is swept at the source, absorption peaks superimposed on the total microwave power will now appear at the detector and can be displayed on an oscilloscope or a strip-chart recorder. The absorption peaks are due to rotational transitions in the molecules of the gas. The peaks at the detector output will be a low frequency ac signal and consequently the output signal will have a poor signal-to-noise ratio due to the $1/f$ noise characteristic of the detector diode. If the microwave source is modulated with a suitable high frequency signal, the low frequency ac signal will be amplitude-modulated on this high frequency carrier, thus greatly improving the signal-to-noise ratio¹⁸.

When a static electric field is applied in the Stark cell, a spectral line will split into two lines due to the Stark effect. From the frequency separation of these two lines, the electric field strength, the moment of inertia, and the quantum numbers of the transition, the values of the dipole components along three principal axes of the molecule can be calculated. This was first done by Dakin, Good and Coles¹⁹ on the linear triatomic $O = C = S$ molecule.

Instead of the source modulation mentioned above of Gordy and co-workers, the Stark-voltage can be modulated and applied to the cell as a high frequency, square wave voltage, with the same sensitivity improvement as a result. This idea was introduced by Hughes and Wilson²⁰ in 1947, and is still the leading construction principle today.

1.4. Volume of work on dipole moment determinations

To end this general and historic introduction some general remarks based on statistics made by McClellan²¹ may be in place. The volume of published work on dipole moments rose from almost nothing in 1920 to nearly 0,2% of the papers reported in Chemical Abstracts in 1932. After a minimum of 0,05% in 1944 a peak of 0,25% appeared in 1949 much depending on the advent of microwave spectroscopy. Still in 1960 the quantity of papers was over 0,1% of the enormous chemical literature.

2. GENERAL CONSIDERATIONS ON GAS PHASE DIPOLE MOMENT MEASURING METHODS.

If dipole moments are to be determined with accuracy the measurements have to be carried out with the molecules far apart in order to avoid interactions between the molecules, i.e. the determinations must be made in the gas phase and the gas pressure should preferably be below atmospheric pressure.

2.1. Molecular beam method

In a molecular beam apparatus the molecules under investigation are very far apart which is inherent in the beam technique. As mentioned before a typical gas pressure in microwave spectroscopy is 10^{-3} mmHg. With larger pressures the microwave absorption lines will broaden and this pressure broadening will obscure the hyperfine structure of the spectra, and the accuracy of frequency measurement will decrease.

2.2. Dielectric temperature variation method

The dielectric temperature variation method based on the Debye equation (3) has mainly been used for measurements of liquids and solutions of polar substances in non-polar solvents. However, a few measurements have been made on gases, but are restricted to substances with vapour pressures as high as a few hundred mmHg. The dipole moments resulting from these measurements on gases are usually in very good agreement with the moments from microwave spectroscopy. The gas phase measurements have been considered to be experimentally difficult to carry out so most measurements with the dielectric temperature variation method are made in solutions.

2.3. Microwave spectroscopy

The microwave spectroscopy and the molecular beam techniques are both spectroscopic methods which implies that dipole moments derived from these methods refer to a specific electronic and vibrational state in the molecule. The dipole moment also refers to a single isotopic species of the molecule. If the substance to be determined is not pure, this is of little importance in spectroscopic methods. Dielectric methods are bulk methods which means that the calculated dipole moment is an average of moments in different vibrational states and an average over various isotopic species. This is a principal difference between spectroscopic and dielectric methods. Comparison of dipole moments determined by the two methods shows that this difference usually is of no great practical importance. The difference is unlikely to exceed one percent at ordinary temperatures. However, in the case of bulk dielectric methods great care must be taken to ensure that the purity of the sample is the highest possible.

The effective dipole moment measured with dielectric methods may sometimes be an average of quite different dipole moments if the compound can exist in more than one conformational isomer. In this case the resulting dipole moment can be rather misleading. Such a case will be revealed from the microwave spectrum and the dipole moments of the individual isomers can be determined.

2.4. Accuracy of dipole moments measured with different methods

The molecular beam electric resonance method is capable of giving values of dipole moments with an accuracy of 0,02 percent. The precision is 0,001 percent or even better. With this high accuracy it is possible to measure the dipole moment of different vib-

rational states of a molecule. These very small uncertainties are due to the very small spectral line widths and to the fact that the electric field can be kept uniform and very well defined.

In microwave spectroscopy an accuracy of one percent or less can nearly always be attained in the calculated dipole moment. Also the orientation of the dipole moment within the molecule is obtained. In spite of the fact that microwave spectroscopy and the molecular beam technique both make use of the Stark effect of rotational transitions, the former method gives a larger uncertainty, which is partly due to a certain inhomogeneity in the electric field in the Stark cell.

From the dielectric temperature variation methods, based on the Debye equation, the dipole moment can be evaluated from the slope of this function with an uncertainty within one percent under favourable conditions.

2.5. Limiting factors for different methods

The molecular beam method, being the most accurate method for determining dipole moments, is unfortunately also the most limited method. The technique can only be applied to a very limited group of molecules. The molecules have to be diatomic or possibly triatomic. Larger molecules will have a great number of states, so that the population in each state will be small. Thus the sensitivity will diminish as the population decreases. Also the cost of a molecular beam apparatus is high.

Microwave spectroscopy measurements are sometimes complicated by a very high density of lines causing interference between the Stark lines. Available transitions may show an insensitivi-

ty of one (or two) dipole component for the Stark effect. The result will be only one accurate component of the dipole moment and consequently the total dipole moment can be quite uncertain. If a nucleus has a nuclear quadrupole moment this is coupled to the rotation of the molecule. This interaction which shows up as hyperfine multiplets can complicate the spectrum and misleading values of the Stark effect can be obtained. Since the dipole moments depend on the electric field strength in the Stark cell, the applied voltage and the cell geometry have to be carefully measured. Voltage measurements are easily done accurately but the cell dimensions are often crucial²². In addition, the electric field is inhomogeneous at the edges of the septum and this will cause a Stark line broadening. These difficulties are usually avoided by Stark effect measurements on OCS, whose dipole moment is known very accurately. In this way the effective electrode spacing is calibrated.

Another limitation is that the molecule must not be too large. Partial information on molecules with 30 atoms has been achieved, but 15 atoms in the molecule seems to be an upper limit for a complete analysis of the structure.

Some of the theoretical limitations of the dielectric temperature variation methods have already been discussed, such as the averaging of the dipole moment over different vibrational states and over different conformational isomers. Also the thermal distribution of vibrational states of the molecule has to be relatively constant over the actual temperature interval. Considering the experimentally determined quantities: capacitance, temperature, and gas density, the latter seems to be the quantity which imposes limitations on the experimental accuracy. Capacitance and temperature can more easily be determined with small uncertainties.

3. GAS PHASE MEASUREMENTS VERSUS MEASUREMENTS IN SOLUTIONS

Since dielectric measurements in solutions are much more easier to perform than gas phase measurements, most dipole moment determinations which have been published, have been made in solutions. The first to point out that interactions occur between a polar solute and a non-polar solvent was Miller^{23,24,25}. In solutions fairly high concentrations of the solute are used which also leads to an interaction between the polar solute molecules via their permanent dipoles. This is accounted for by extrapolation to zero concentration. However, the interaction between solute and solvent molecules is more serious. This results in dipole moment values which differ from gas phase measurements and which show a dependence of the nature of the solvent, though the solvents are non-polar. This can be explained generally as an interaction between the permanent dipoles of the solute and the induced dipoles of the solvent molecules. Many attempts have been made to give a relation which could be used to correct these deviations. In addition to dipole interaction, molecular complexes of different kinds and hydrogen-bonding can complicate the picture even more. Gas phase measurements avoid these pitfalls, although at the cost of much greater experimental difficulties. Table 1 illustrates the differences in dipole moment derived from gas phase and solvent measurements and also the solvent effects.

Table 1. Dipole moment (in Debye units) variations between gas phase and different solvents²⁶.

Compound	Gas phase	C ₆ H ₆	Dioxane	Solvent CCl ₄	n-Hexane	CS ₂	C ₆ H ₅ NO ₂
CH ₃ CN	3,97	3,47	3,56	3,43	3,35	3,21	-
CH ₃ OH	1,69	1,68	1,93	1,72	-	-	-
C ₆ H ₅ Cl	1,72	1,58	1,65	1,62	1,61	1,50	-
CS ₂	0	0,03	-	0,4	0,08	-	1,21

4. GENERAL CONSIDERATIONS ON THE DIELECTRIC TEMPERATURE VARIATION METHOD FOR GAS PHASE MEASUREMENTS

4.1. Quantities to be measured in the Debye equation

Recalling the Debye equation (3) and rewriting it slightly we get

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi N \alpha}{3} + \frac{4\pi N \mu^2}{9kT} = A + \frac{B}{T} \quad (6)$$

If the dielectric constant, ϵ , and the density, ρ , for a gas is measured as a function of the absolute temperature, T , the molar polarization, P , can be calculated and plotted against $1/T$. From the slope, B , of this plot, the dipole moment, μ , of the gas can be calculated as

$$\mu = \sqrt{\frac{9kB}{4\pi N}} \quad (7)$$

4.2. Frequency dependence of the dielectric constant

The Debye equation is derived from electrostatic considerations but usually an alternating electric field is used for the measurement of the dielectric constant. Consequently the frequency dependence of the dielectric constant or the molar polarization which is closely related, have to be considered. The "static" value of the dielectric constant is the same as for low frequencies. When the frequency is increased the dielectric constant remains constant until the period of the alternating field becomes comparable with the relaxation period of the molecule. This relaxation period is dependent of the molecular inertia. Increasing the frequency further results in a phase difference bet-

ween the electric field and the permant dipole direction, which leads to a decrease in the dielectric constant. For smaller molecules the dielectric constant may be constant up to several gigahertz. Crain et.al.⁴³ have measured for instance the dielectric constant of acetone at 9,4 GHz. The result was identical as expected with the "static" value since the first rotational transition of acetone is at 15 GHz.

4.3. Definition of the dielectric constant and permittivity

The dielectric constant measurements as required by the Debye equation are based on measurements of capacitance according to the definition

$$\epsilon' = \frac{C}{C_0} \quad (8)$$

where ϵ' is the dielectric constant or the relative permittivity, C_0 is the capacitance of a capacitor with no dielectric, i.e. evacuated, and C is the capacitance with a dielectric. This is true for an ideal capacitor, but in reality there are always losses which can be represented as an equivalent resistance, R , in parallel with the capacitance. The major part of these losses arises from the dielectric, so a complex permittivity, ϵ^* , has to be defined as

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (9)$$

ϵ'' is called the loss factor, not to be confused with the dissipation factor or loss tangent

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \omega RC \quad (10)$$

The loss tangent is frequency, f , dependent since the angular frequency, ω , is

$$\omega = 2\pi f \quad (11)$$

At very low frequencies and with a gaseous dielectric, the loss factor is usually vanishingly small, so that

$$\epsilon^* = \epsilon' \quad (12)$$

At zero frequency ϵ' becomes the static dielectric constant.

4.4. Determination of the gas density

Determination of the gas density is sometimes made directly with e.g. the Dumas method²⁷. However the usually preferred indirect method is to measure the gas pressure with a mercury manometer or some other means²⁸, and calculate the gas density from the equation of state of an ideal gas. Deviations from the ideal gas law may introduce an error in this latter method. This possible error decreases with decreasing gas pressure.

4.5. Temperature range

In order to attain an accurate value of the dipole moment, the molar polarization should be measured over a range of temperature so wide as possible. However, this temperature interval is subject to several limitations of both theoretical and practical character. If conformational isomers are present and their average moment should be measured, the temperature range should be small, especially if the equilibrium between the isomers is

very dependent on the temperature. Among the practical limitations it can be mentioned that a precision capacitance measuring cell must not be subject to excessively large temperature excursions in order to maintain the mechanical stability of the cell. An upper temperature limit is often set by thermal decomposition of the substance to be measured. On the other hand the lower temperature limit is set by the vapour pressure of the compound.

5. EXPERIMENTAL DIELECTRIC METHODS FOR GAS PHASE MEASUREMENTS

5.1. Resonant circuits

The most employed methods of measuring dielectric changes in the gas phase can be divided in three groups: the heterodyne beat method, resonance methods, and bridge methods. The two first mentioned types of methods provide accurate means of capacitance determinations provided that the dielectric loss is negligible. This is usually the case with gas phase measurements. Bridge methods are in principle not sensitive to dielectric losses since in bridges both capacitive and resistive balancing can be arranged. However, the heterodyne beat method and resonance methods all use resonance in resonant circuits as a reference state, and as this resonance will be less well defined in lossy circuits, accuracy will be impaired.

In a series resonant circuit with a capacitance, C , an inductance, L , and a resistance, R_S , which represents the losses, as in figure 1A, the resonant frequency, f_0 ,

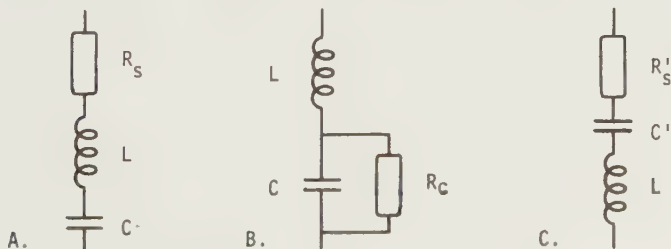


Figure 1. Series resonant circuits.

will be given by

$$f_0 = \frac{1}{2\pi\sqrt{LC}} \quad (13)$$

The sharpness of the resonance is described by the quality factor, Q , given by

$$Q = \frac{X}{R_S} \quad (14)$$

where X is the reactance of either the capacitance or the inductance. This relation clearly illustrates the influence of the losses on the sharpness of the resonance. The quality factor is also given by

$$Q = \frac{f_0}{\Delta f} \quad (15)$$

where Δf is the bandwidth between the frequencies where the circuit attenuates 3 dB as compared with the resonant frequency.

Figure 1B shows a series resonant circuit with a capacitance with a lossy dielectric represented by R_C . This parallel combination of C and R_C can be transformed in a series combination C' and R_S' as in figure 1C. Since C' is not equal to C , the resonance frequency will shift according to (13). If, however, R_C is large the resonance frequency will be given approximately by (13).

The relation (13) is also approximately valid for a parallel resonant circuit (see figure 2) provided that the equivalent parallel resistance R_p is very large. Also here R_p is representing the dielectric and other losses. In this case

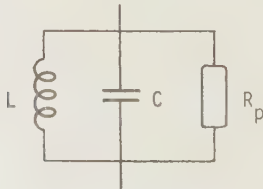


Figure 2. Parallel resonant circuit.

the quality factor is given by

$$Q = \frac{R_p}{X} \quad (16)$$

which shows that a large R_p , equivalent to small losses, will give a large Q .

5.2. Heterodyne beat method

5.2.1. The principle of the method

The principle of the heterodyne beat method is illustrated by figure 3. The reference oscillator is usually crystal controlled on a fixed frequency at a few megahertz. The frequency generated

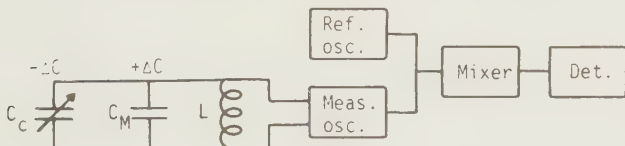


Figure 3. Block schematic of the heterodyne beat method.

by the measuring oscillator is determined by the inductance L and the capacitances C_C and C_M . With (13) the values of these components are chosen to give the same frequency as the reference oscillator. The mixer produces the sum and the difference between the two oscillator frequencies. The frequency sum is suppressed in a low-pass filter and only the frequency difference is passed on to the detector. Simple earphones have often been used as a detector.

5.2.2. Evaluation of the dielectric constant

To perform a capacitance measurement, the measuring capacitor C_M is evacuated and the compensating capacitor is adjusted to give a zero frequency beat. If a gas is introduced as a dielectric into the measuring capacitor, the capacitance will rise from a value C_0 to C_1 . The compensating capacitor can now be used to retune the circuit so that the frequency of the measuring oscillator increases until the zero beat is detected again. With no dielectric losses involved the definition of the dielectric constant (8) can be used:

$$\epsilon' = \frac{C}{C_0} \quad (8)$$

Since only pure capacitances are considered in gas phase measurements the notation on the dielectric constant is dropped. In this case we obtain

$$\epsilon = \frac{C_1}{C_0} \quad (17)$$

which also can be written

$$\epsilon - 1 = \frac{C_1 - C_0}{C_0} \quad (18)$$

The capacitance change ΔC as read on the compensating capacitor is equal to the difference $(C_1 - C_0)$ and consequently

$$\epsilon - 1 = \frac{\Delta C}{C_0} \quad (19)$$

In gas phase measurements the quantity $(\epsilon-1)$ is usually preferred instead of ϵ . This is convenient since ϵ differs very little from unity.

5.2.3. Drawbacks of the method

The heterodyne beat method has been extensively used for gas phase measurements²⁹⁻³⁹ in consequence of the sensitivity of the method. However, the sensitivity can not be increased beyond a limit set by the inherent frequency instability of the oscillator. This frequency instability is due to random variations in circuit parameters if the short-term instability is considered. Long-term frequency drift is caused by component ageing and environmental changes. With extremely careful construction and thermostating a short-term frequency stability of approximately one part in 10^6 per hour may be obtained.

The heterodyne beat method has a drawback which has not been fully considered in earlier measurements. This is the tendency of the two oscillators to lock in when their frequencies are quite close to each other. This synchronization of the oscillators will appear when the screening between them is not sufficient. The lock-in shows up as a broad zero beat causing errors in the capacitance measurements⁴⁰. Some workers^{29,33} have got round this difficulty by introducing a third, fixed audio frequency oscillator. The variable measuring RF oscillator is thus not tuned to zero beat, but instead to the frequency of the audio oscillator, and the two audio frequencies are compared e.g. with the help of the Lissajous pattern on an oscilloscope screen. Lock-in is easily overcome with modern solid state circuitry. Opto-electronic coupling between the oscillators and the mixer would also be a simple way of ensuring perfect isolation.

Another source of error which may be appreciable is lumped inductance effects. These effects on the capacitance measurement are small at the usually employed frequencies of a few megahertz, but

compared with the high precision necessary in gas phase measurements, these effects can be substantial³⁹.

Due to stray capacitances, the vacuum capacitance, C_0 , required by (8) can not be measured in this circuit. Consequently the apparatus has to be calibrated with carbon dioxide, which is commonly used, or some other suitable standard gas. It should also be noted that random variations in the stray capacitances make up a considerable proportion of the errors which set the precision limit of this method.

5.2.4. Accuracy of the method

The accuracy of the method can be estimated from equation (13). Differentiation of this relation yields

$$\frac{df}{f_0} = - \frac{1}{2} \frac{dC}{C} \quad (20)$$

The capacitance C is composed by C_M and C_C (see figure 3). Supposing a working frequency of 1 MHz, C_M will have a value of a few hundred picofarads and C_C about 10 pF. Thus the resonating capacitance C is approximately equal to the measuring capacitance, C_M . With the relative short-term frequency stability of $1:10^6$, the relative capacitance resolution will be $2:10^6$. The absolute capacitance resolution will consequently be around 300 aF (aF, attofarad equals 10^{-18} farad), provided that the errors mentioned above are negligible and that the compensating capacitance is carefully calibrated.

5.2.5. Application at microwave frequencies

The heterodyne beat principle has also been applied at microwave frequencies by Crain⁴¹ using two Pound oscillators⁴², a diode mixer, and an intermediate frequency amplifier inserted before the detector circuits. With this equipment very good measurements on gases have been made⁴³.

5.3. Resonance methods

Many resonance methods have been devised. Most of them are used for measurements of liquids. The working principle is illustrated by figure 4.



Figure 4. Simplified schematic of a resonance apparatus.

A fixed-frequency crystal controlled oscillator is loosely inductively coupled to a resonant circuit. Resonance is indicated by a vacuum tube voltmeter in order to minimize loading of the circuit. The Q of the resonant circuit must be high to permit a sensitive detection of the very small capacitance differences encountered in gas phase measurements⁴⁴. The measuring capacitance, C_M , and the compensating capacitance, C_C , are used in the same manner as described before. However, Le Fèvre⁴⁵ has modified the circuit

by using a variable frequency oscillator instead of the crystal controlled oscillator (see figure 5). The capacitances C_M and



Figure 5. Simplified schematic of a modified resonance apparatus.

C_C , and an inductance are chosen to give an oscillator frequency equal to the resonating frequency of the quartz crystal X . The inductance, L , and the capacitance, C , are also tuned to this frequency. Thus with no quartz crystal the VTVM will indicate a relatively broad maximum. With the series resonating quartz crystal in the circuit there will be a very sharp minimum. Since quartz crystals can be produced with very high quality factors, a very well defined reference frequency may be obtained.

5.4. Bridge methods

The third group of methods for measuring dielectric changes in the gas phase is bridge methods. An impedance bridge can be sketched as in figure 6.

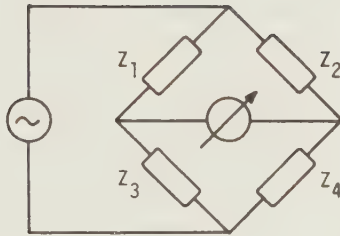


Figure 6. An impedance bridge.

"Common" capacitance bridges have pure resistances in two adjoining arms and some series or parallel arrangement of resistors and capacitors in the remaining two arms. However, these common types of capacitance bridges are far too insensitive for measurements on gaseous dielectrics. The sensitivity limit is mainly set by stray capacitive coupling between the bridge arms and between the arms and ground. By suitable shielding these coupling effects can be minimized and a sensitivity comparable with that of the heterodyne beat method has been achieved⁴⁶⁻⁴⁸. Lovering and Wiltshire⁴⁹ have attained a sensitivity of the order of one p.p.m. with an extensive shielding technique.

5.5. Transformer bridge

5.5.1. Development of the transformer bridge

The stray capacitive coupling affecting the bridge balance can be eliminated in transformer bridges. This type of bridges is by no means new and forerunners to the modern transformer brid-

ges are the "Differential-induktor" of Elsas⁵⁰ in 1888 and the "differential transformer" of Trowbridge⁵¹ in 1905. It was Blumlein⁵² who was the first in 1928 to devise the modern transformer bridge principle with closely coupled inductive ratio arms for the comparison of impedances. Starr⁵⁶ in 1932 described the 3-winding transformer bridge with unity turns ratio as equal arms. With this arrangement of Blumlein and Starr any stray impedance or voltage which is developed in one winding is reflected in the other because of the mutual inductance between the tightly coupled ratio arms. This basic principle of the transformer bridge has been used and described by several workers⁵⁴⁻⁶⁵. Some work concentrated on the development of the bridge for measuring capacitance and conductance with limited accuracy over a wide frequency range⁵⁵. The possibility of measuring very small capacitances with the transformer bridge was not fully revealed before the work of Thompson^{58,60} at the National Standards Laboratory of Australia. His work was aiming at high accuracy measurements of small capacitors. This was realized partly due to the invention of the cylindrical cross capacitor as a calculable standard^{66,67}. Also the work of Cutkosky and others⁶¹ at the National Bureau of Standards in the U.S. is an important contribution to the understanding of this powerful technique. The work of these standard laboratories is naturally directed towards the measurement of absolute capacitance. Thus the absolute unit of capacitance is known with an accuracy of approximately one part per million. Dunn⁶⁵ at the National Research Council of Canada has also constructed a transformer bridge with similar capabilities.

5.5.2. Principles of the bridge

An equivalent circuit of a simple transformer bridge with equal ratio arms is depicted in figure 7.

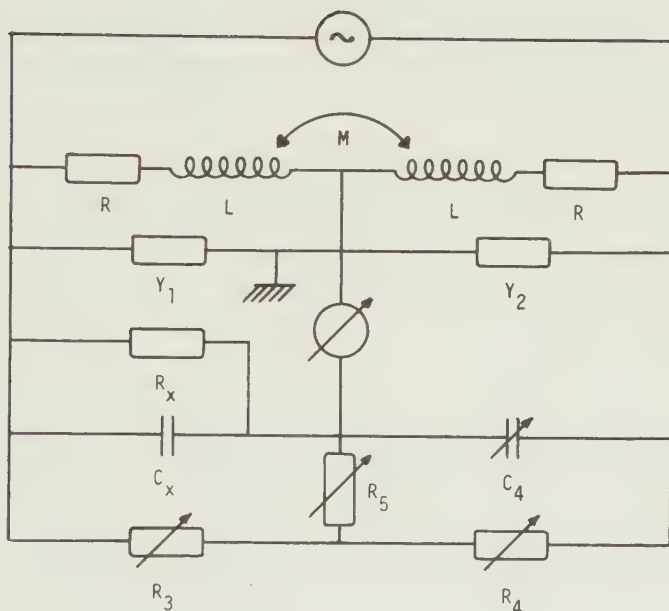


Figure 7. Equivalent circuit of a simple transformer bridge with equal ratio arms.

For this circuit Cole and Gross⁵⁵ have derived an approximate expression (21) for the balance relation,

$$\frac{(1/Z_3) - (1/Z_4)}{1/2(1/Z_3) + (1/Z_4)} = (Y_1 - Y_2) \cdot \frac{R + j\omega(L - M)}{1 + 1/2(Y_1 + Y_2)[R + j\omega(L - M)]} \quad (21)$$

where the impedances Z_3 and Z_4 are including R_x , C_x , C_4 , R_3 , R_4 and R_5 according to figure 7. The T-network of R_3 , R_4 and R_5 was used to attain an almost linear, direct reading of the unknown

conductance G_x . R_5 permits a simple means of shifting the range of the conductance. The two ratio arms comprise equal inductors, L , with series resistances, R . Stray admittances to ground are designated Y_1 and Y_2 . M is the mutual inductance between the inductors.

If expression (21) is taken into consideration it can be seen that if $M = L$ and $R = 0$ the right hand side of the relation will be zero. This implies that the bridge balance will be independent of Y_1 and Y_2 . It is this fact which makes the transformer bridge a powerful tool for measuring small capacitances.

The practical realization of a very close coupling between the inductors ($M \approx L$) and a diminutive resistance ($R \approx 0$) requires that the inductors are wound on a large toroidal core of high permeability with a small number of turns of a conductor with a large cross-sectional area. The balancing of the bridge can be made in principally two ways. To illustrate this, an even more simplified equivalent circuit of a transformer bridge can be found in figure 8.

In this figure the conductance balancing components have been omitted, and the equal ratio arms have been considered as generators with series impedances Z_1 and Z_2 . These generators supply emf's of opposite phase. When the bridge is balanced and consequently no current is flowing through the detector, the currents I_3 and I_4 through the capacitors C_3 and C_4 respectively must be equal,

$$I_3 = I_4 = U_3 \omega C_3 = U_4 \omega C_4. \quad (22)$$

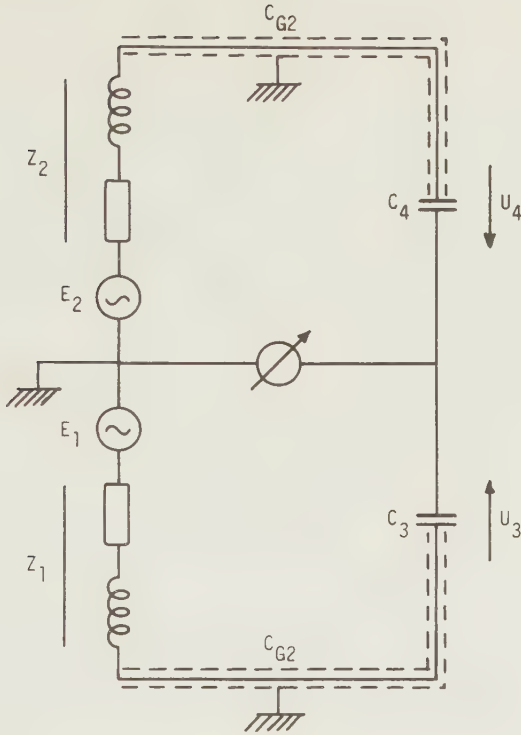


Figure 8. Simplified equivalent circuit of a transformer bridge.

Hence,

$$\frac{U_3}{U_4} = \frac{C_4}{C_3} \quad (23)$$

Z_1 and Z_2 are representing the resistances and leakage reactances in the ratio arms. If these impedances are negligible compared to $1/\omega C_{G1}$ and $1/\omega C_{G2}$, the cable capacitances to ground, then

$$\frac{E_1}{E_2} = \frac{C_4}{C_3} \quad (24)$$

From this balance condition (24) it is obvious that capacitive balance can be obtained by varying either one of the capacitances or one of the emf's. Referring to figure 7, it can be seen that capacitive balance can be effected by varying C_4 . If this capacitor is of a switched decade type, a coarse balance is obtained. By adding further decades a finer balance can be achieved. This will be an expensive method if accuracy is required, since ten precision capacitors per decade is needed. The capacitive balancing can also be attained by varying the emf as mentioned. This is done by providing one of the ratio arms with taps, so the ratio can be adjusted. However, the division is limited by the number of turns, which should be kept low. The insertion of additional transformers will easily overcome this limitation. The transformer bridges at NSL, NBS and NRC, already mentioned, and also commercial bridges from General Radio and Wayne Kerr, all use variations of this basic principle with adjustable ratio arms. With an extensive electromagnetic shielding technique it is possible to attain emf ratios which equal the turns ratios to 1 in $10^{7.60}$.

The conductance balance can be obtained by the same technique as for providing capacitive balance. A conductance standard is usually made as a T-network of resistors or a combination of resistors and capacitors.

The generator is usually inductively coupled to the transformer bridge through a primary winding as shown in figure 9.

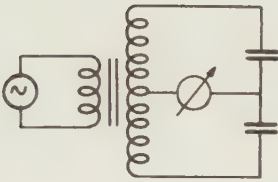


Figure 9. 3-winding transformer bridge.

5.5.3. Three-terminal capacitors

For the measurement of small capacitances or small capacitance differences, three-terminal capacitors have to be used. Figure

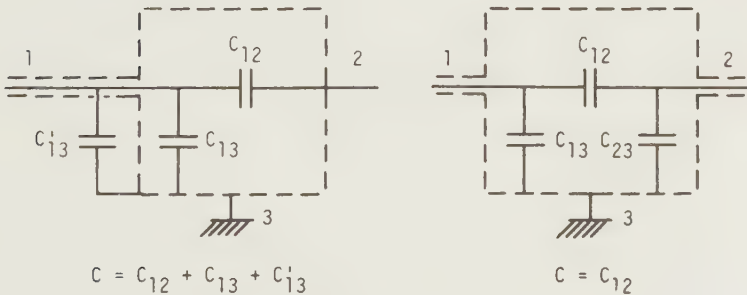


Figure 10. Capacitance of a two-terminal (left) and three-terminal capacitor (right).

10 illustrates the difference between a two-terminal and a three-terminal capacitor measured in a transformer bridge. The capacitance in a two-terminal

capacitor includes the capacitance to the grounded shield, C_{13} , and the cable capacitance, C'_{13} . The latter is of course dependent on the length of the shielded cable. The capacitance of a three-terminal capacitor, measured in a transformer bridge, is completely independent of ground capacitances. This fact can be used in constructing capacitors with very small capacitances as in figure 11. The



Figure 11. Small three-terminal capacitor.

capacitor plates can only "see" each other through a small hole in a grounded wall. In this way extremely small capacitances can be realized. Even if C_{12} (figure 10, left) was removed, the ground capacitances C_{13} and C'_{13} would remain. Since these ground capacitances may have quite large values it would be impossible to construct a small two-terminal capacitor.

If three-terminal capacitors are placed in a transformer bridge as in figure 12, it can be seen that the cable capacitances to ground, C_{G1} and C_{G2} , will be in parallel across the windings and that C_{G3} appears across the detector. C_{G1} and C_{G2} will introduce a loading on the transformer, but will not affect the balance of the bridge, if the resistances and leakage inductances in the ratio arms are kept small, which has already been discussed. C_{G3} will not have any effect on the bridge balance, but the sensi-

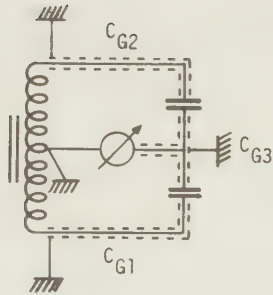


Figure 12. Transformer bridge ground capacitances.

vity of the detector may decrease if this ground capacitance becomes large. Consequently the bridge will only measure the very well defined capacitance of the three-terminal capacitor.

6. CONSTRUCTION OF A SENSITIVE TRANSFORMER BRIDGE

6.1. General considerations

In the previous section the principles of the transformer bridge have been outlined. Constructing e.g. an eight decade transformer ratio bridge is a very exacting and specialized task⁶¹. In this work a simple transformer bridge with a 1:1 ratio has been used in combination with a capacitance substitution circuit, thus avoiding the complicated ratio transformer division, but taking advantage of the outstanding features of the transformer bridge.

If the balance equation (21) is taken into consideration, it can be seen that not only for the condition $R=0$ and $M=L$, the right hand side will be zero, but also when the admittances Y_1 and Y_2 are equal, the right hand side will be zero, i.e. the bridge can be balanced. These admittances represent the distributed capacitances in the windings, the shunting ground capacitances of the cables and also pure resistances arising from insulation leakage and dielectric losses. With gaseous dielectrics and careful design these resistances can be kept extremely high and thus the conductances are negligible. In decade ratio bridges with division transformers it is impossible to keep the shunting capacitances equal. This is possible to achieve, however, with equal transformer arms and a complete symmetry of the bridge.

Thus great care has been used to ensure complete electrical, mechanical, and thermal symmetry in the construction of the bridge. Many other small errors will then also cancel with much improved stability of the bridge as a result.

6.2. The transformer

At the time of the beginning of this work, suitable toroid cores were not available in Sweden. Therefore two E-shaped cores with a cross area of 12x15 mm were chosen as transformer cores. The core material was a ferrite from Philips called Ferroxcube 3E1. The contact surfaces of the two core halves were precision ground together to ensure a good fit. The halves were bonded together with a small amount of epoxy cement. The bridge arms were bifilar wound with each 200 turns of enameled copper wire with a diameter of 0,6 mm. The bifilar winding technique ensures a very good symmetry indeed, with respect to resistance, distributed capacitances and number of turns. The DC resistance of each arm is 0,7 ohms. The primary of the transformer was wound with 50 turns of the same wire as the secondary. Thus the primary voltage will be transformed four times. The bridge arms were provided with taps at 20 turns from the ground point in the center. These taps are used for obtaining a reference signal to the phase sensitive detector, which will be described later.

6.3. Capacitance substitution technique

The bridge has been used with a capacitance substitution technique which is illustrated schematically in figure 13.

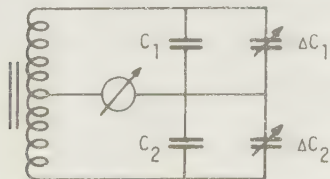


Figure 13. Transformer bridge with substitution capacitances.

Two fixed vacuum capacitances, C_1 and C_2 , have small variable capacitances, ΔC_1 and ΔC_2 respectively coupled in parallel. If a gaseous dielectric is admitted to C_1 its capacitance is increased and bridge balance can be restored by decreasing ΔC_1 or increasing ΔC_2 . However, it is preferred to decrease ΔC_1 , since if ΔC_2 is used, a small error may be introduced if the turns ratio is not exactly unity. Using ΔC_2 as compensation also increases the load on the transformer. Since only gaseous dielectrics are involved in this work, the increasing load is of no concern at all. The maximum capacitance increase is 0,1 percent in the case of carbon dioxide (1 atm). The capacitance C_2 is mechanically and electrically identical with C_1 , but is solely used as a reference and to make the bridge completely symmetrical. For the same reason ΔC_2 is identical with ΔC_1 .

6.4. Substitution capacitances

6.4.1. Design considerations

The two fixed measuring capacitors have each a capacitance of approximately 100 pF. Introduction of a gaseous dielectric as e.g. carbon dioxide at atmospheric pressure will increase the capacitance by approximately 0,1 pF. Other actual dielectrics will make even lesser changes, so 0,1 pF was considered to be a suitable range for the substitution capacitances. A concentric cylinder arrangement was chosen as the best capacitance geometry, with an inherent low temperature coefficient and because small mechanical eccentricities will cause negligible capacitance changes⁶⁸. However, it would be very impractical to construct a small, variable cylinder capacitor of 0,1 pF with a linear variation. Good linearity implies that the ratio between outer and

inner cylinder radii should be small to avoid varying end effects. Unfortunately a small ratio will make a large capacitance, which is evident from equation (25) which gives the capacitance, C , of a cylinder capacitor with the length, l , the outer and inner radii, r_1 and r_2 respectively. ϵ is the dielectric constant of the dielectric and ϵ_0 is the permittivity of vacuum.

$$C = \frac{2\pi\epsilon\epsilon_0 l}{\ln r_1/r_2} \quad (25)$$

The addition of two capacitances, C_1 and C_2 , to the variable capacitances, ΔC_2 , as shown in the circuit in figure 14 offers a convenient solution of the problem.

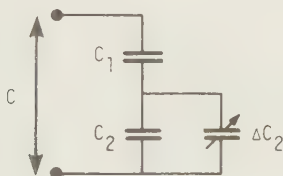


Figure 14. Circuit for scaling down the range of a variable capacitance.

By choosing appropriate values for C_1 and C_2 a considerable scaling down of the variable capacitance ΔC_2 is possible, which can be seen in equation (26),

$$dC = \left(\frac{C_1}{C_1 + C_2} \right)^2 d\Delta C_2 \quad (26)$$

if an infinitesimally small capacitance range, dC_2 , is considered. For finite changes a minor correction term, $\Delta C_2/(C_1+C_2)$, appears in the denominator in equation (27).

$$\Delta C = \left(\frac{C_1}{C_1+C_2} \right)^2 \frac{1}{1 + \frac{\Delta C_2}{C_1+C_2}} \cdot \Delta C_2 \quad (27)$$

The circuit in figure 14 has to be enclosed by a grounded shield to permit three-terminal measurements in a transformer bridge. The capacitance from the interconnecting leads between C_1 , C_2 and ΔC_2 to ground will affect the bridge balance contrary to the other cable capacitances. This fact is illustrated by figure 15.

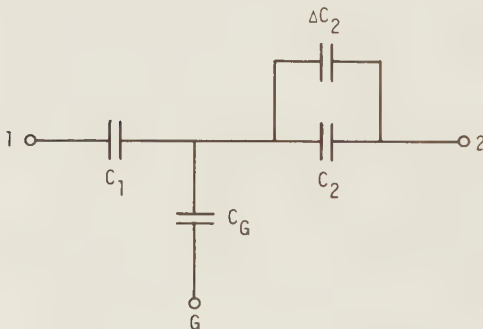


Figure 15. The scaling down circuit as a T-network.

Transforming the T-network in figure 15 to a delta-network yields,

$$C_{12} = \frac{C_1(C_2 + \Delta C_2)}{C_1 + C_2 + \Delta C_2 + C_G} \quad (28)$$

and

$$\Delta C_{12} = \frac{k_1 \cdot \Delta C_2}{k_2 + \Delta C_2} \quad (29)$$

where $k_1 = \frac{C_1(C_1 + C_G)}{k_2}$ and $k_2 = C_1 + C_2 + C_G$

If the ground capacitance C_G is made small and the construction is made so that C_G will be very stable, then the ground capacitance will not complicate the circuit very much. The complete capacitor arrangement in the bridge is shown in figure 16.

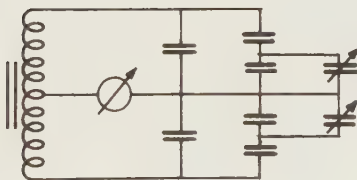


Figure 16. Transformer bridge with complete capacitor arrangement.

6.4.2. Construction details

The construction of the variable capacitor can be seen in principle in figure 17 and in detail in figure 18. An inner stainless steel rod, which has been precision ground, slides through a

bronze bearing. The spring-loaded rod can be positioned by a precision micrometer screw. The rod is pushed into a cylinder of stainless steel with a ground inner surface. The cylinder length is long compared to the length of the inner rod protruding into the cylinder. In this way varying end effects in the lower part of the cylinder can be kept very small. To define the electric field at the top of the cylinder a grounded stainless steel disc has been inserted between two insulating ceramic discs. Thus the clearance between the stainless steel disc and the inner rod is only 0,5 mm. The stainless steel disc fits into a hole in a separating wall in the capacitor housing. Electrical connections are made directly to the outer cylinder and via the bronze bush to the inner rod. Consequently the bush is not lubricated, but made of a special bronze to prevent seizing. The total capacitance is 7 pF and it can be varied $\pm 1,3$ pF. The micrometer screw

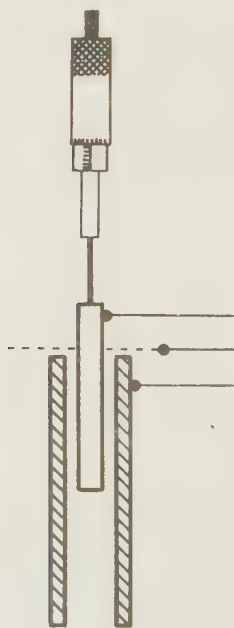


Figure 17. Schematic construction of the variable capacitor.

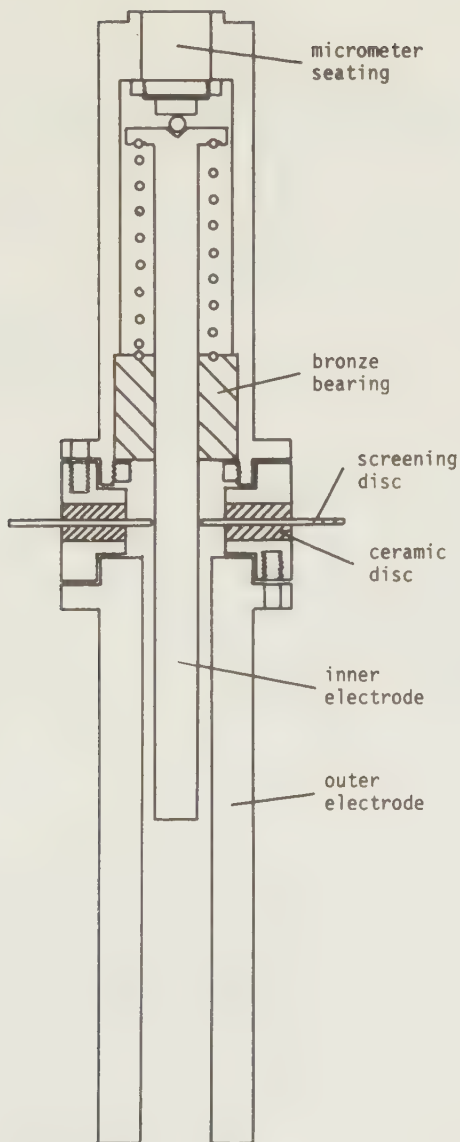


Figure 18. Construction details of the variable capacitor.

has a travel of 25 mm and has a resolution of 0,0005 mm. The first four figures are read digitally and the two last figures are read on a vernier scale. In consequence, the capacitance resolution will be 50 aF.

6.4.3. "Scaling down" capacitors

One of the fixed capacitors which are used for scaling down the capacitance range (C_2 in figure 14) is a General Radio type 1403 Standard Air Capacitor with a capacitance value of 100 pF. This is a plate-type capacitor with good stability. The other fixed capacitor (C_1 in figure 14) should have a value of about 17 pF to give a suitable scaling down, with the ground capacitance taken into account. The capacitor was constructed with concentric cylinders of polished, chrome-plated brass. This capacitor geometry was chosen by virtue of its low temperature coefficient and its insensitivity to mechanical eccentricities. The cylinders are held in place by thin Delrin plates and are housed in a brass can.

6.4.4. Mounting

The dual assembly of the variable capacitors C_1 and C_2 is rigidly built into a heavy duralumin can, divided into suitable, screened compartments. Duralumin was chosen as construction material on account of its mechanical rigidity and its high specific heat capacity. The container is thermally insulated in a very thick polyurethan foam case, which was cast in situ. The high heat capacity of the duralumin in conjunction with the very low thermal conductivity of the polyurethan foam, provides a large thermal time constant and hence a good thermostat action for the assembly. Two protruding rods of acrylic glass are used to operate the two micrometer screws in order not to upset the thermostat action.

6.4.5. Calibration

Each of the two capacitor circuits has a resultant capacitance value of 9 pF and the variation range is 0,1 pF. Thus the capacitance resolution will be 2 aF. The capacitance as a function of the value read on the micrometer screw is a rather linear relationship. This relation is described by equation (29). If the constant k_2 is sufficiently large compared to ΔC_2 , the relation will be linear. In this case this is almost true, hence an additional second order term is sufficient for an adequate description of the relation.

In order to determine the deviation from a linear relationship in these two capacitor systems, a calibration was made with a General Radio Capacitance Measurement Assembly, Type 1620-AP. The resolution of the bridge in the actual capacitance range is limited to 10 aF by the number of decades. The sensitivity is excessive so an external reference standard capacitor with a value of 100 pF can be added to provide a seventh decade above the bridge. However, such a reference standard capacitor was not available. This difficulty was avoided by reversing the calibration procedure. Thus the GR-bridge was set to specific values and bridge null was adjusted with the capacitor system to be calibrated. The variable capacitor system was consequently employed as a means of interpolating below the bridge decades.

The calibration data points were fitted to a least square parabola,

$$y = a_0 + a_1x + a_2x^2 \quad (30)$$

with typical constant values,

$$a_0 = 9,2905695 \text{ pF}$$

$$a_1 = 4,26342 \cdot 10^{-3} \text{ pF/mm}$$

$$a_2 = - 2,641 \cdot 10^{-6} \text{ pF/mm}^2$$

The calibration was checked periodically and was found to be very stable. The calculations were performed on a Hewlett-Packard Calculator 9810 with a modified hp-program 09100 - 70815.

6.5. Capacitance measuring cells

6.5.1. General demands

The capacitance measuring cells (C_1 and C_2 in figure 13) are the most crucial parts in the whole measuring system. With a total capacitance of 100 pF, a capacitance stability as low as 2 aF is desired. This is a stability of two parts in 10^8 which should be maintained for at least one hour. Since only relative capacitance measurements are considered, a long term stability of several parts per million can be accepted. The variables affecting the stability of the capacitance during a measurement period of one hour are mainly pressure and temperature. Pressure variations of one atmosphere will alter physical dimensions, but as long as these changes are small and reproducible, they can be accounted for. Temperature variations arising from pressure changes are difficult to avoid, but if no capacitance-temperature hysteresis effect is present, such temperature variations are of little concern. The measuring cell must also withstand the mechanical handling associated with e.g. ampoule changes.

6.5.2. Choice of capacitor type

The computable cross capacitor is obviously a good choice⁶⁹ but is not easily handled e.g. in conjunction with a LKB 7602/03 A

precision thermostat. The second choice will be a conventional cylinder capacitor, which also may give satisfying results as will be shown. A cross-section of a suitable concentric cylinder capacitor is shown schematically in figure 19. As mentioned be-

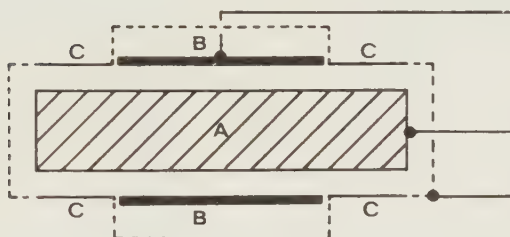


Figure 19. Schematic cross-section of a cylinder capacitor with guard cylinders.

fore small deviations from the concentric shape of the inner cylinder A and the outer cylinder B will have very little effect on the capacitance.

6.5.3. Guard electrodes

In order to define the dielectric measuring volume between A and B, guard cylinders C have been incorporated in the construction⁵⁴. Thus the homogeneous electric field between A and B will be continued between A and C. In this way fringing fields between A and B are avoided. To accomplish this guard effect, the guard cylinders C must have the same potential as B. This can be achieved by connecting the capacitors as in figure 20. When the bridge is balanced, no current will flow through the detector and con-

sequently the outer electrodes B will assume ground potential. The guard electrodes are directly grounded, so B and C are both at ground potential.

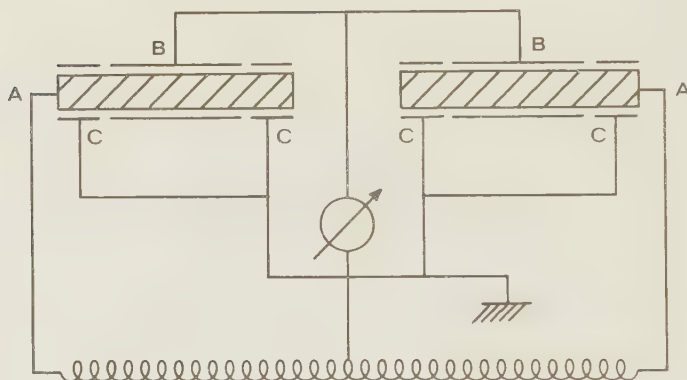


Figure 20. Schematic showing the connection of the guard electrodes in the transformer bridge.

It will be seen in figure 20 that the guard capacitance from A to C will be connected in shunt with the windings which entails that this capacitance will not alter the bridge balance. The capacitance between the guard cylinders C and the outer capacitor cylinder B can be seen to lie in parallel with the indicator, so again, the bridge balance will not be affected by this capacitance.

Reverting to figure 19 it can be noted that the grounded electrostatic shield (dashed lines) can also serve as a vacuum-container. This vacuum housing must be constructed so it can be immersed in a water thermostat.

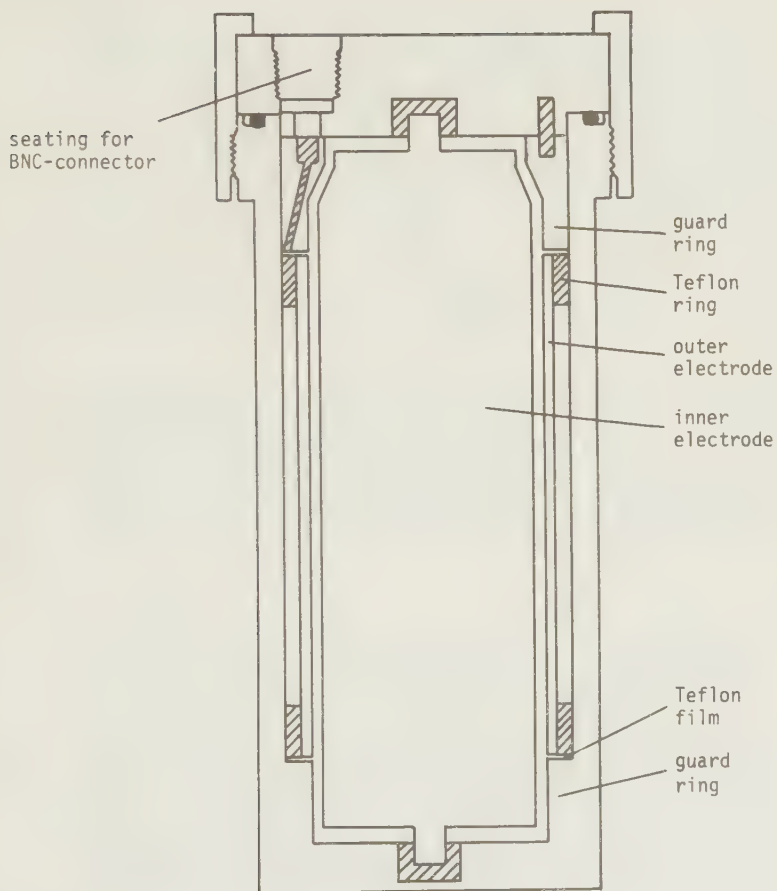


Figure 21. Construction details of a capacitance measuring cell.

6.5.4. Construction details of the first constructed capacitors.

In figure 21 the details of the first constructed capacitance measuring cell can be seen. The inner cylinder, A, made of stainless steel, is suspended by insulating pieces of PTFE between the bottom and the lid of the heavy stainless steel container. The outer cylinder, B, is held in place radially by annular PTFE spacers and axially by very thin PTFE washers. The annular spacers are grooved to permit pressure equalization. The PTFE washers are made very thin (0,1 mm) with the object of not upsetting the homogeneity of the electric field.

The inner and outer cylinders are very carefully turned to correct dimensions in order to achieve a close capacitance match between the two cells. This capacitive matching should preferably be done to a few hundredths of a picofarad or at least within the range of one of the scaled-down variable capacitors.

6.5.5. Disadvantages of the first capacitors.

However, this capacitance measuring cell failed to work properly. When subjected to pressure and temperature variations, the capacitance of the cell was noted to be liable to a hysteresis effect. In addition this effect was very irregular. The behaviour had several causes. The outer cylinder was held in place by PTFE details as mentioned above. The difference in the coefficient of linear thermal expansion for PTFE and stainless steel produced too much mechanical stress on the cylinder with temperature variations. Since PTFE is susceptible to cold-flow it is likely to cause irregular, irreversible mechanical stresses.

Another problem encountered with this measuring cell was the tendency of the PTFE details to dissolve ketones. As a result, the evacuating of the cell became a very time-consuming procedure. This problem was augmented by the liberal use of silicon rubber O-rings as vacuum seals in the measuring cell and in the adjoining vacuum system. The tendency of the polymers to dissolve the vapour to be measured was serious, as it was planned to calculate the gas density in the cell from volume and mass determinations.

6.5.6. Construction details of the second capacitors.

The difficulties encountered in the first constructed capacitance measuring cell were avoided in the second version, which proved to operate in an acceptable manner. It was decided to make the capacitor self-supporting to dispense with the need for various insulating spacers and to replace the rubber O-rings with indium O-rings.

Pyrex (Jobling) borosilicate glass was chosen as the supporting material for the capacitor. Trials were made with vacuum deposition of aluminium, silver, gold and rhodium. Rhodium was found to make a very good bond to the glass. The other metals had a slight tendency to peel off. With the vacuum deposition apparatus available, it was extremely difficult to produce sufficiently thick films of rhodium due to the high evaporation temperature of rhodium, about 2300°C . Then fired-on metal coatings were tried and a silver paint from Degussa, Frankfurt am Main, type 314E, was found to have a very good adhesion to the Pyrex glass. It was fired on at a temperature of 550°C .

A cross section of the capacitor can be seen in figure 22.

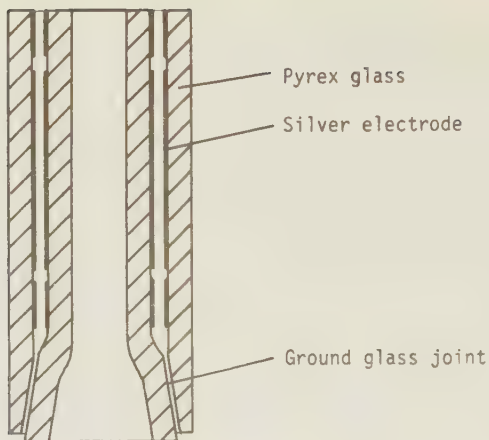


Figure 22. Cross section of the silvered glass capacitor.

The silvered glass capacitor is made of two concentrically arranged glass tubes with a small clearance between them. The tubes are provided with a ground joint in one end. The outer tube has a thin fired-on silver coating on the inner surface. The inner tube is silver coated on the outside in three sections, one electrode surface and two guard sections at the ends. Two narrow non-silvered spacings are separating the sections. The electrical connections to these sections are made with platinum wires from the inside through small holes in the glass. The platinum wires are secured by the silver. The overall length of the assembly is 125 mm and the mean diameter is 35 mm. The capacitance is about 100 pF.

After polishing and cleaning the silver surfaces, the assembly was matched to a second assembly with regard to the capacitance. This was done by a slight trimming of the edge of the inner electrode area with nitric acid. After matching, the inner cylinder was gently pressed into the outer cylinder to create a slight seizure between the carefully ground joining surfaces. This procedure was carried out in polarized light so serious mechanical stresses

could be detected and relieved.

The assembly was mounted in a vacuum can. A screen is provided in the can to shield the connecting wires from each other. The wires were fed through the lid with coaxial glass-to-metal seals, soldered in place in the lid. These seals were preferred to the vacuum BNC-connector used in the first measuring cells. Although these BNC-connectors are helium leak-tested for vacuum-tightness they contain both PTFE and a silicon rubber O-ring.

The can is made of heavy brass, nickel-plated on the outside. The inner surfaces of the can and also the lid are gold-plated. The lid is bolted to the can and fitted with a M-shaped groove to accommodate an indium O-ring for vacuum-sealing.

The various indium O-rings used in the apparatus were produced by extrusion of an indium string in a small press with exchangeable dies with different diameters. A pressure of about $2 \cdot 10^8 \text{ N/m}^2$ produces a soft string of indium, which should promptly be chopped into suitable lengths. A slanting cut gives a large, sticky area which is immediately stuck together with the surface in the other end.

A Kovar tube joins the lid with a glass vacuum system containing an electromagnetically operated ampoule breaker. This can be seen in figure 23. The ampoule is a sealed small glass tube which is seated in the bottom of the ampoule chamber. When a current pulse is applied to the solenoid, the glass-sealed iron rod will be drawn into the solenoid and the ampoule is broken. Ampoules are inserted and withdrawn through the top of the ampoule chamber. The sealing between the gold-plated brass cap and the glass flange is also made with indium O-rings.

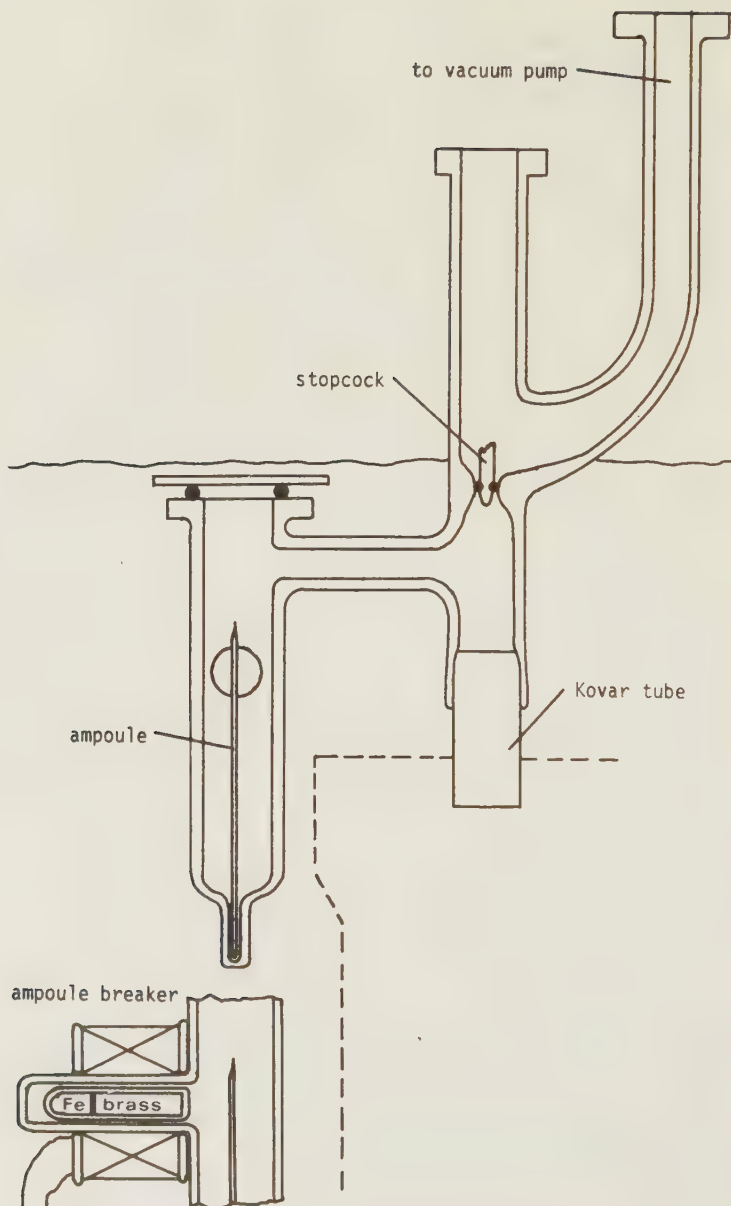


Figure 23. Glass vacuum system.

Small indium O-rings were tried in the stopcock seating but were found unsuitable owing to their inelasticity. Rubber O-rings were used instead and due to their small size and the very small exposed surface the amount of ketone vapour dissolved in the rubber was negligible.

6.5.7. Losses in a glass dielectric.

Measurements of the vacuum capacitance of these cells did show a relatively large conductance of about 200 pS (equals $2 \cdot 10^{-10} \Omega^{-1}$). From previous experience an expected value would be less than 1 pS. It was found then, that a small fringing electric field was passing parts of the Pyrex glass support in the non-silvered spacing between the inner active electrode and the lower guard, due to insufficient shielding. Consequently, an error will be introduced in measurements of dielectric constants. This can easily be seen in figure 24.

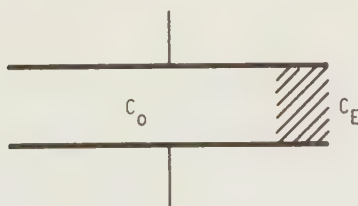


Figure 24. Schematic representation of losses in the glass support.

The gaseous dielectric can not fill the part of the capacitor occupied by the glass dielectric. If equation (19) is considered an error capacitance, C_E , is entered in the denominator, thus producing

$$\epsilon - 1 = \frac{\Delta C}{C_0 + C_E} \quad (31)$$

an error in $(\epsilon-1)$ which can be seen in equation (31).

This problem was dealt with by an indirect determination of the fraction of the capacitance occupied by the lossy Pyrex glass dielectric, i.e. the additional capacitance, C_E . A piece of Pyrex glass, taken from the same length of tubing as the inner tube of the silvered measuring glass capacitors, was silvered in the middle section both inside and outside. This test capacitor with glass dielectric only was then measured on a General Radio Capacitance Measurement Assembly, Type 1620-AP. At 25°C the following result was obtained:

$$C = 112,751 \text{ pF}$$

$$G = 74250 \text{ pS}$$

Since the conductance of 200 pmho in the measuring capacitor can be attributed entirely to the lossy glass dielectric, proportionality yields

$$C_E = 0,304 \text{ pF}$$

In this way an accurate correction could be applied to the vacuum capacitance, C_0 .

The conductance can be attributed to the losses in the glass dielectric due to the high surface resistivity of the glass. For the Pyrex (Jobling) glass used the specified surface resistivity is $10^{13} \text{ ohm}\cdot\text{cm}$ at 50% relative humidity. The resistivity can be assumed to be more than two orders of magnitude larger in vacuo. Considering the capacitor geometry a leakage resistance larger than 10^{13} ohms should be expected. This resistance corresponds to a conductance of less than 0,1 pS. Kanno⁷⁰ has measured the conductance of Pyrex glass capacitors with comparable leakage paths and has found a conductance of 0,1 pS.

6.5.8. Temperature control.

The assembly of the two measuring capacitors with adjoining glass vacuum system is placed in a LKB 7603A water thermostat controlled within $\pm 0,001^{\circ}\text{C}$ by a LKB proportional controller 7602A. The cooling water for the LKB thermostat is thermostatically controlled by a second thermostat of simpler design. The temperature range of the thermostat is 22°C to 60°C . It was found that maximum stability in the measuring cells was obtained in the range 25°C to 45°C , so all measurements have been made in this temperature interval. The temperature was read on a calibrated thermometer with a certified accuracy of $0,03^{\circ}\text{C}$.

6.6. Generator

The transformer bridge is supplied with an AC voltage by a transistorized generator. The frequency determining stage in the generator is a LC-oscillator with a tuned collector circuit. The positive feedback to the base to sustain oscillation can be adjusted by means of a potentiometer to give the best possible waveform. The oscillating frequency is about 10 kHz. The choice of frequency will be discussed later. The AC voltage is inductively coupled to a buffer amplifier and the amplified voltage is fed to the transformer bridge. The primary of the transformer is tuned to 10 kHz. The voltage supplied to the bridge is about 60 volts peak-to-peak. An obvious way of increasing the sensitivity of the bridge is to raise the bridge voltage. However, there is a practical upper voltage limit set by the size of the transformer and by increasing loading errors.

6.7. Indicator

A simple indicator for the transformer bridge would be an arrangement of an AC amplifier followed by a rectifier and a meter. However, it is not useful to increase the amplifier gain beyond a certain level where the noise becomes too large, since it will result in a poor signal to noise ratio.

6.7.1. Noise sources.

Let us shortly review the different origins of noise, since noise suppression is an important part of the system design. Noise can be divided into several categories, namely resistance noise, shot noise, 1/f-noise and environmental noise. The resistance noise⁷¹ (thermal noise, Johnson noise) is due to the thermal fluctuations of matter and consequently the noise current, I_{NR} , is related to the absolute temperature, T , (32).

$$\overline{I_{NR}^2} = \frac{4kT\Delta f}{R} \quad (32)$$

In this relation, where k is the Boltzmann constant and R the noise generating resistance, we note that the noise is related to the frequency bandwidth and hence the spectral distribution will be flat and for this reason the noise is usually said to be "white". The resistance noise is the dominating noise in resistances at not too low frequencies.

Shot noise⁷² is generated in p-n-junctions of solid-state devices. The conduction in a p-n-junction is a random mechanism, quantized by the charge of the electron, e . The mean squared shot noise current,

$\overline{I_{NS}^2}$, is given by

$$\overline{I_{NS}^2} = 2Ie\Delta f \quad (33)$$

where the current I may be e.g. an emitter current or a diode current. The Δf -dependence makes also this noise type a white noise.

The origin of $1/f$ -noise is not completely understood, but can be found in e.g. semiconducting materials. As the name implies, this type of noise increases with decreasing frequency. $1/f$ -noise is usually the dominating noise species below 100 Hz. Thus the $1/f$ -noise or drift in DC-amplifiers is very large.

Environmental noise is made up of many types of noise from a wide variety of noise sources. To mention a few, the mains, sparks from motors, switches, and ignition systems, radiation from fluorescent lamps and thyristor controls, radio and TV-stations, are all man-made noise. Temperature and humidity fluctuations constitute a second group of noise sources. The spectral distribution of the environmental noise has also an $1/f$ character which can be seen in figure 24 A.

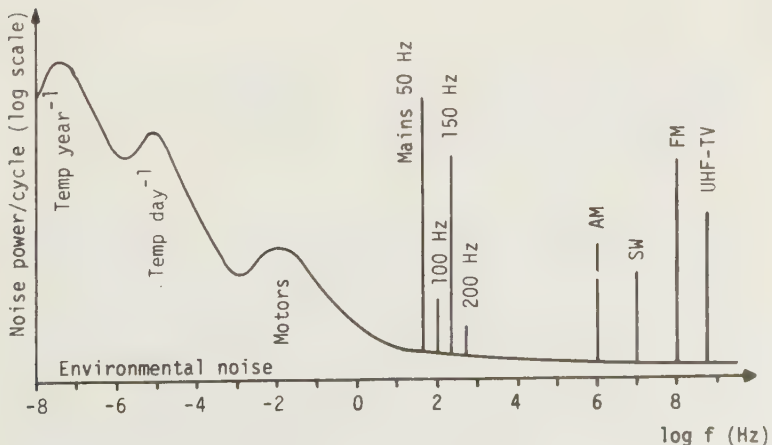


Figure 24 A. Typical environmental noise spectrum.

6.7.2. Noise level reduction

Considering environmental noise, it would be favourable to place the information from the transformer bridge in a quiet part of the noise spectrum, e.g. at 10 kHz. With this choice of operating frequency, $1/f$ -noise will be avoided. Resistance noise and shot noise can be minimized by keeping the frequency bandwidth as small as possible according to (32) and (33). The necessary bandwidth is governed by the frequency of the information, in this case the error signal from the transformer bridge. Since the information, i.e. the amplitude variations of the error signal, has a very low frequency, a bandwidth of one hertz would be suitable. If this low information frequency had not been transferred to 10 kHz, it would have been buried in $1/f$ -noise.

A carrier frequency of 10 kHz can also be accepted with regard to inductive reactances in the transformer bridge. The inductive reactance, X_L , is given by

$$X_L = 2\pi fL \quad (34)$$

where f is the frequency and L the inductance. At 100 kHz the lead inductive reactances would be appreciable and at 1 MHz accurate measurements are not possible.

6.7.3. Operating frequency compared with the frequency region of dielectric dispersion.

From a physico-chemical point of view, the low frequency of 10 kHz is very satisfactory. The operating frequency must not have a period comparable with the relaxation period of the molecules

to be investigated. The group of substances of primary interest in this work is the ketones. The first rotational transition of acetone is at 15 GHz and that of trans-2-butanone is at 12 GHz. Consequently six orders of magnitude are separating the operating frequency and the rotational transition frequencies.

6.8. System considerations

Let us describe the measuring system in large, generalized blocks as in figure 25.

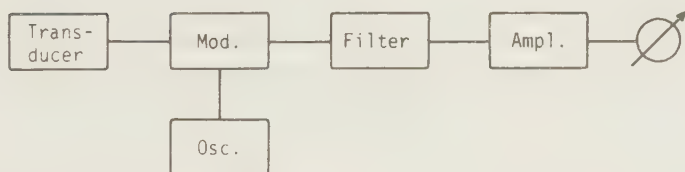


Figure 25. A generalized block schematic of a measuring system.

In this case the transducing and modulating functions are made in the transformer bridge. The error signal from the bridge is amplitude modulated on a carrier supplied by the oscillator, i.e. the generator supplying the AC voltage to the bridge. Thus the operating frequency of 10 kHz is simply determined by the bridge generator frequency. As concluded above, the filter and the amplifier should have a bandwidth of one hertz. This would require an effective Q-value of 10.000. Even if this Q-value had been possible to realize, a slight oscillator drift relative to the

centre frequency of the narrow filter, would have introduced a serious amplitude error.

6.8.1. Phase detection technique.

With modern phase detection technique (synchronous detection, lock-in technique) it is possible to overcome the difficulties mentioned above^{73,74}. Phase detection uses the principle that cross-correlation of a signal with the signal itself produces a DC-voltage irrespective of the integrating time, while cross-correlation of random noise with a periodic signal produces a voltage going to zero with increasing integrating time. In practice the cross-correlation is made by a phase detector.

The first to use this powerful technique was the radio astronomer Dicke⁷⁵ in 1947. His phase-detecting radiometer made it possible to measure with precision the radiation temperature of different astronomical objects. Phase detection is a must for detecting weak NMR signals, so NMR spectroscopists adopted this technique very early.

The function of the phase detector is outlined in figure 26.

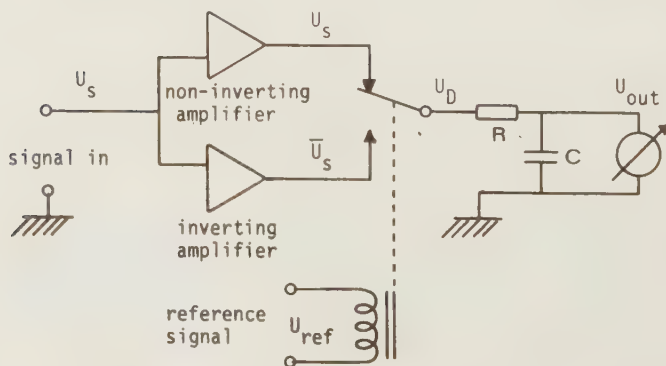


Figure 26. Schematic illustration of the function of a phase detector.

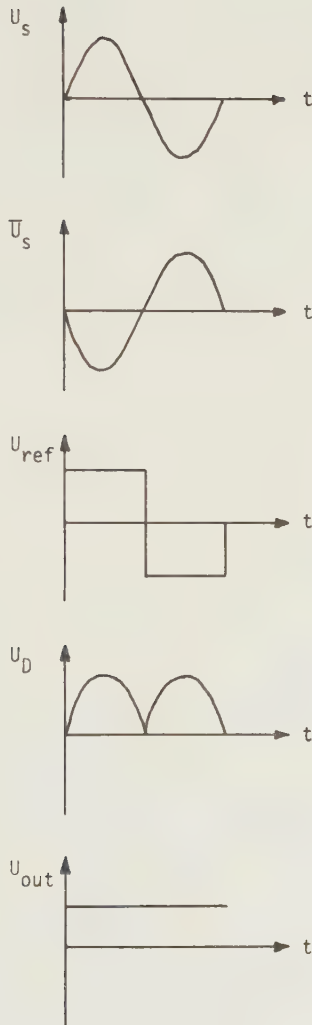


Figure 27. Different waveforms in the phase detector.

The reference signal, U_{REF} , is a square wave voltage with the same frequency and phase as the input signal, U_S . The reference signal operates a switch, connecting the signal to be detected for the first 180 degrees of the period and then the inverted signal for the next 180 degrees to the low-pass filter. The detected signal, U_D , will look like a full-wave rectified signal. The voltage U_D is then passed on through a low-pass filter. Thus the output signal, U_{OUT} , contains only the DC component of the detected signal. The DC voltage is proportional to the amplitude of the input signal. Since the noise is not correlated to the reference signal it will average to zero. The bandwidth of the phase detector depends on the low-pass filter and hence will be given by

$$\Delta f = \frac{1}{2\pi RC} \quad (35)$$

The practical realization of the phase detector can be very sophisticated, utilizing modern digital technique⁷⁶. However, the classical circuit with a transformer as phase splitter and with diode switching seems to be the most stable for precision measurements.

6.8.2. Phase detection applied to the measuring system.

Figure 28 shows how the phase detection is incorporated in the measuring system.

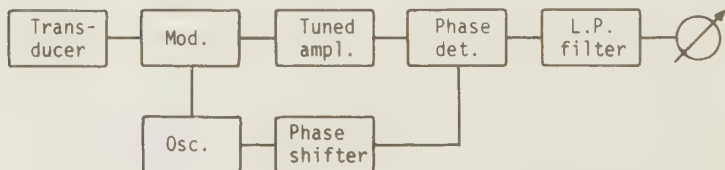


Figure 28. Measuring system with phase detection.

As can be seen in figure 28 the reference signal to the phase detector is derived from the oscillator (bridge generator) and a phase shifter has been added so that the phase of the reference signal can be adjusted exactly to the phase of the signal to be detected. Since the bandwidth of the system is determined by the low-pass filter, the amplifier for the bridge signal need not be tuned, at least in principle. However, a tuning with moderate Q is practical, since the tuning prevents overloading the phase detector by reducing the noise level.

6.8.3. Complete block schematic.

In figure 29 the complete capacitance measuring system can be seen in a more detailed block schematic.

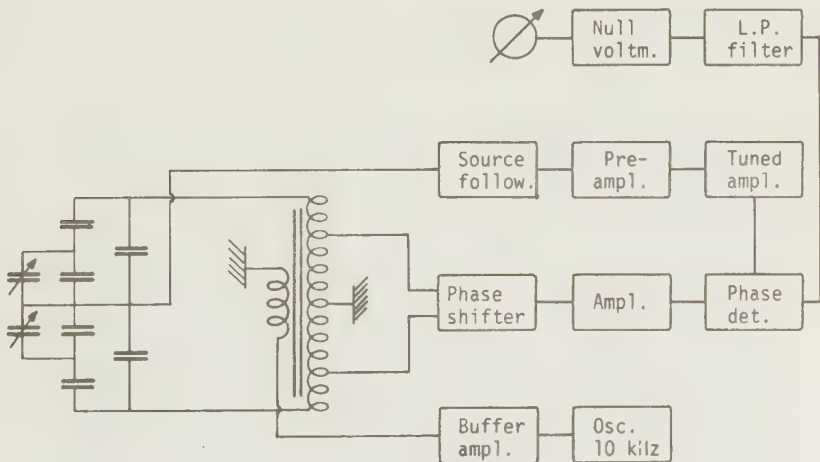


Figure 29. Complete block schematic of the capacitance measuring system.

The bridge impedance seen by the amplifier is about 100 k Ω . Hence a reasonable value of the amplifier input impedance should be 50 to 100 times larger. For this reason a source follower precedes the detector amplifier proper. The error signal from the bridge is then amplified in a low noise preamplifier. The tuned amplifier is of conventional design, using a frequency-selective feedback. The effective Q-value is about 15. The phase-sensitive detector is succeeded by a low-pass filter. Different capacitors can be switched in, giving a bandwidth of one hertz or less. The read-out of the error signal from the bridge was done on a DC null voltmeter (Hewlett Packard, type 419A).

6.8.4. Environmental noise level reduction.

Much work has been spent on reduction of the noise level in the measuring apparatus. Some aspects of noise reduction have already been discussed, but some further points will be dealt with.

Considering the electronic circuitry, great care has been taken in the choice of components. This has led to a substantial reduction of the noise level as compared to the first prototype.

In order to attenuate the environmental noise, a screened measuring room has been employed. The screened room is placed inside an ordinary room. The construction material in the screened room is wood and wire netting (1 wire/cm). The room is double-screened, i.e. it consists of an outer screen and an inner screen insulated from each other. The spacing between the screens is five centimeters. The attenuation of a single screen increases with increasing wire mesh number, wire diameter and volume of the room. Double-screening gives an appreciable additional attenuation, increasing with the two first mentioned factors and with increasing screen spacing. The screened room was found to have insufficient attenua-

tion below one megahertz and above 50 megahertz. This is due to the fact that electromagnetic radiation is to be reflected by this type of screen. However, the reflecting power is low at low frequencies and at high frequencies the mesh size is not negligible compared to the wavelength so a RF leakage will result. The low attenuation at low and high frequencies proved to be a serious drawback, since the frequencies of most sources of interfering radiation were actually low and high. Low frequency sources were fluorescent lamps and other in-house sources. High frequency interfering signals came from FM-transmitters and UHF-TV-stations. Some VHF and UHF signals also seemed to be enhanced by the screened room acting as a resonator with resonating frequencies given by

$$f = C_0 \sqrt{\left(\frac{\alpha}{2a}\right)^2 + \left(\frac{\beta}{2b}\right)^2 + \left(\frac{\gamma}{2c}\right)^2} \quad (36)$$

where C_0 is the velocity of electromagnetic radiation, a, b, c are the dimensions of the room, and α, β, γ are integers¹¹². The high and low frequency attenuation was then increased by lining the outer screen with 0,025 mm aluminium foil. In addition to the better reflecting power a material absorption will take place within the foil owing to eddy current losses, resulting in an appreciably higher attenuation also at high and low frequencies. With this improvement the screened room provided sufficient attenuation to permit measurements of small capacitance differences. It should be noted that the separate screens in the room must not be connected in more than one place. The shielded and filtered mains intake should also be fed through the screens at the junction. The mains is filtered by inserting a shielded full transformer and a few shielded sections of series inductances and parallel capacitances with gradually decreasing LC-products. The screen junction is grounded with a heavy copper strap, and all grounding inside the room is made to the screen junction. It is also essential that radiating

units used inside the room (e.g. the bridge generator) are properly shielded.

The room outside the screened room is thermostated to within 1°C and the screened room to within $0,1^{\circ}\text{C}$ with contact thermometers, fans, heating elements and a water cooling unit.

7. PERFORMANCE OF THE CAPACITANCE MEASURING SYSTEM

7.1. General

7.1.1. Sensitivity.

The sensitivity of the indicator is more than adequate, so the (capacitance) resolution is determined by the variable substitution capacitor. The capacitance resolution is 2 aF which is equal to a relative sensitivity of 2 parts in 10^8 .

7.1.2. Overall stability.

The overall stability can be defined in several ways depending on whether short term or long term stability is considered. However, the most important factor affecting the stability is the type of handling of the measuring cells.

If the capacitance measuring cells are left undisturbed in the thermostat, a short term drift of less than 5 aF can be observed in a period of one hour. The drift in capacitance over 24 hours seldom exceeds 25 aF.

When the measuring capacitors were used for the measurement of the dielectric constant for some non-polar gases, the gases were admitted to the measuring capacitor at a pressure of one atmosphere, the capacitor was then evacuated, filled again and so on. The measuring cells were, however, never removed from the thermostatic bath. For a measuring period of one month the drift was less than 100 aF, corresponding to a relative drift of less than one part per million.

In the measurement of polar substances, loading the measuring cell with ampoules demanded the removal of the capacitor assembly from the thermostat. As a result of this handling, the measuring capacitor could occasionally deviate a few parts per million in capacitance.

7.1.3. Effects of atmospheric pressure and humidity.

Since the variable substitution capacitors are not hermetically sealed, the effects of varying atmospheric pressure and humidity have to be considered. Suppose that the duration of a determination of a dielectric constant is one hour. Experience shows that pressure changes larger than 0,2 mb per hour rarely occur. This pressure change will introduce an error of one part in 10^7 which is equal to a capacitance error of 0,7 aF. Taking the scaling down factor of 1:25 into consideration, 0,03 aF is the error affecting the capacitance measurement. During most measurements pressure changes have not been detected.

A water-vapour partial pressure of 7 mmHg is a quite normal content of water-vapour in the air in the measuring room. This water-vapour has a $(\epsilon-1)$ -value of 10^{-4} . Since the water-vapour pressure is about one hundredth of the total air pressure, the effective $(\epsilon-1)$ -value is 10^{-6} . A change of the water-vapour content with 10 percent introduces an error of one part in 10^7 , which is scaled down 1:25 yielding a capacitance error of 0,03 aF. However, the variable capacitor is not ventilated, and as gas diffusion is slow, such rapid changes as 10%/hour are unlikely inside the capacitor.

7.1.4. Effects of temperature variations.

The effect of temperature variations on the variable capacitors can be calculated, assuming a coefficient of linear expansion of

16 ppm/ $^{\circ}\text{C}$ for the stainless steel and that the measuring room temperature variations of $0,1^{\circ}\text{C}$ are reduced to a tenth by virtue of the thermal insulation. This corresponds to a variation of $0,16$ ppm in a 7 pF capacitor, which equals 1 aF. When the 1:25 scaling down is taken into account, $0,04$ aF results.

Temperature variation effects on the measuring capacitors can readily be estimated from the $\pm 0,001^{\circ}\text{C}$ temperature stability of the thermostatic bath and the $3,3$ ppm/ $^{\circ}\text{C}$ coefficient of linear expansion of the Pyrex glass. The measuring capacitance value of 100 pF yields $0,7$ aF. This estimation and also the preceding ones are worst case calculations assuming one-sided influence on the symmetrical bridge arrangement.

7.2. Performance tests

To check the performance of the capacitance meter, the dielectric constants of some non-polar gases were measured. National Bureau of Standards has tabulated recommended values of dielectric constants of the reference gases helium, hydrogen, oxygen, argon, air, nitrogen and carbon dioxide⁷⁷. Of these gases, hydrogen, nitrogen and carbon dioxide were chosen for the performance test owing to the low, medium and high dielectric constants respectively. (A few measurements on argon were also made.)

7.2.1. Purity of the test gases.

The gases were supplied by Alfax AB, Malmö. The purity of argon and nitrogen was analysed by the supplier. The purity of carbon dioxide and hydrogen was controlled to lie within certain limits. The analytical methods used were mainly gas chromatography combined with mass spectrometry and dew point methods. See table 2.

Table 2. Purities of the gases used in the performance tests.

Gas	Purity (%)	Impurities (v.p.m.)					Notes
		A	H ₂	N ₂	O ₂	H ₂ O	
A	99.9996	-	<0,4	1,5	<0,3	2,1	Uncertainty ± 0,2 v.p.m.
CO ₂	99.998			8	2	5	Traces of CO and C _n H _m
H ₂	99.9997		-	0,5	0,5	2	
N ₂	99.9995	1,0	0,5	-	1,1	2,0	

7.2.2. Experimental procedure.

The measuring cells were normally kept evacuated to a pressure of less than $5 \cdot 10^{-4}$ mmHg, as read on a Pirani vacumeter. If the cells were left standing, exposed to the atmosphere, difficulties with adsorbed gases were encountered. Especially adsorbed water showed a slow desorption on evacuating.

The measuring procedure began with reading the vacuum capacitance. Several readings were taken during half an hour to check for any possible drift. The gas to be measured was then admitted to the measuring capacitor. This was done slowly so that the temperature in the capacitor was not disturbed more than necessary. A period of about half an hour was then allowed to permit the gas to come to temperature equilibrium. Readings were then taken until a stable value of the capacitance was obtained. A precision barometer was read several times. The temperature of the measuring cell in the thermostat was also determined.

7.2.3. Evaluation of results.

The capacitance readings were converted to ΔC -values in picofarads with a hp 9810 calculator as mentioned before.

Since the measurements are made at a pressure of one atmosphere, the length, l , of the capacitor will be shortened by the pressure by an amount, Δl ,

$$\Delta l = l - l_0 \quad (37)$$

where l_0 is the length in vacuo. The relation between l and l_0 is given by⁷⁸

$$l = l_0 \left(1 - \frac{1-2\nu}{E} \cdot p \right) \quad (38)$$

where ν is Poisson's ratio, E is Young's modulus and p is the pressure. Radial changes of the capacitor with pressure will not introduce capacitance changes since the ratio r_1/r_2 is not altered, which can be seen in equation (25). Equations (37) and (38) yield

$$\frac{\Delta l}{l_0} = - \frac{1-2\nu}{E} \cdot p \quad (39),$$

Considering equations (1), (22) and (36) we have

$$\frac{p}{C} \cdot \frac{\Delta C}{\Delta p} = - \frac{1-2\nu}{E} \cdot p \quad (40).$$

For $p = 1$ atm and $E = 6,0 \cdot 10^5$ atm at 25°C , and $\nu = 0,20$ given for the Pyrex glass by Jobling, the quantity $p/C \cdot \Delta C/\Delta p$ will be $1,0 \cdot 10^{-6}$. This correction should be applied to the $(\epsilon-1)$ -value calculated with eq.(16).

The C_0 -value was corrected for the glass dielectric as described before. The $(\epsilon-1)$ -value is usually given at a pressure of one atmosphere and a temperature of 20°C . Consequently the $(\epsilon-1)_{t,p}$ -value was converted to $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}}$ with the actual barometric pressure and the measuring temperature.

The pressure read on the barometer was reduced to 0°C and to standard gravitational acceleration, $9,80665 \text{ m/s}^2$. These reductions were based on the local gravitational acceleration, $9,81577 \text{ m/s}^2$. According to recent recalculations the correct local gravitational acceleration is $9,81563 \text{ m/s}^2$ ⁸⁰. However, the old value has been retained, since the change introduced by the correction, $-0,014 \text{ m/s}^2$, is small compared with the experimental uncertainty.

The conversion of the $(\epsilon-1)_{t,p}$ -value to $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}}$ was done with the Clausius-Mosotti relation (1) and Berthelot's equation of state⁸¹. This equation of state is the most appropriate at temperatures about 25°C and at pressures up to two atmospheres. In the case of carbon dioxide it is necessary to use Berthelot's equation of state, but in the case of argon, hydrogen and nitrogen the equation of state of a perfect gas could equally well have been used. The resulting expression is

$$\frac{(\epsilon-1)_{t,p}}{(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}}} = \frac{p}{760} \cdot \frac{293,16}{T} \cdot \frac{\left[1 + \frac{9}{128} \cdot \frac{T_c}{p_c} \cdot \frac{1(\text{atm})}{293,16} \left(1 - \frac{6T_c^2}{293,16^2} \right) \right]}{\left[1 + \frac{9}{128} \cdot \frac{T_c}{760 p_c} \cdot \frac{p}{T} \left(1 - \frac{6T_c^2}{T^2} \right) \right]} \quad (41).$$

The derivation of this expression is given in appendix (1). The critical temperature, T_c , and the critical pressure, p_c , used in the calculations, are given in table 3.

Table 3. Critical temperatures and pressures⁷⁹.

Gas	T_c (K)	p_c (atm)
Argon	151,2	48
Carbon dioxide ⁸²	304,2	72,9
Hydrogen	33,3	12,8
Nitrogen	126,1	33,5

The pressure, p , in (41) should be expressed in millimeters of mercury.

7.2.4. Dielectric constants of argon, carbon dioxide, hydrogen and nitrogen.

The resulting dielectric constants of the individual measurements of the four non-polar gases are presented in table 4 and the results are summarized in table 5.

The limits of error in the measurements are derived in the following manner:

Random error: twice the standard error of the mean of experimental results reduced to 20°C and 1 atmosphere pressure

$$\pm 0,08 \cdot 10^{-6}$$

Table 4. Dielectric constants of four non-polar gases measured at 25°C.

Argon ($\epsilon-1$) _{20°C, 1 atm} · 10 ⁶	Carbon dioxide ($\epsilon-1$) _{20°C, 1 atm} · 10 ⁶	Hydrogen ($\epsilon-1$) _{20°C, 1 atm} · 10 ⁶	Nitrogen ($\epsilon-1$) _{20°C, 1 atm} · 10 ⁶
516,69	921,89	253,79	547,18
516,58	922,29	253,87	547,26
516,68	922,27	253,81	547,35
516,58	922,09	253,71	547,30
516,91	922,16	253,93	547,57
	922,16	253,91	547,17
	922,09	253,77	547,24
	922,34	253,79	547,34
	922,25	253,64	547,29
	922,28	253,74	547,49

Table 5. Summary of the dielectric constant measurements.

Gas	($\epsilon-1$) _{20°C, 1 atm} · 10 ⁶ *	No. of obs.	Limits of error
Argon	516,69 ± 0,12	5	± 0,36
Carbon dioxide	922,18 ± 0,08	10	± 0,32
Hydrogen	253,80 ± 0,06	10	± 0,30
Nitrogen	547,32 ± 0,08	10	± 0,32

* The limits given are twice the standard error of the mean of the experimental results reduced to 20°C and 1 atmosphere pressure.

Estimated maximum systematic errors:

1. Thermometer calibration, $\pm 0,03^{\circ}\text{C}$	$\pm 0,05 \cdot 10^{-6}$
2. Barometer calibration, $\pm 0,1 \text{ mmHg}$	$\pm 0,07 \cdot 10^{-6}$
3. $(p/C) \cdot \delta C / \delta p$ uncertainty $\pm 0,1 \cdot 10^{-6}$	$\pm 0,1 \cdot 10^{-6}$
4. C_0 calibration error, $\pm 0,1 \text{ fF}$	$\pm 0,0005 \cdot 10^{-6}$
5. Error in C_0 -correction, $\pm 1\%$	$\pm 0,02 \cdot 10^{-6}$

The random error given above as an example is valid for carbon dioxide and nitrogen. The random error includes the experimental spread of results arising from the $\pm 0,01^{\circ}\text{C}$ error in reading the temperature, from the $\pm 0,05 \text{ mmHg}$ error in the determination of the pressure, and from the limited resolution in the capacitance measurements. These errors are consequently not included in the systematic errors.

It is believed that the combined effect of all systematic errors of this method does not exceed $\pm 0,3 \cdot 10^{-6}$ in the $(\epsilon-1)$ value.

7.2.5. Comparison of results.

The measurements of the dielectric constants (relative permittivities) of four non-polar gases were made as a performance test of the capacitance meter. In table 6, 7 and 8 the measurements are compared with other data and especially with the NBS recommended values. Most of the data have been compiled by Dunn⁶⁹. The original data have been converted to the reference state of 20°C and 1 atmosphere pressure if necessary. The limits of error listed in the tables are taken from the original references. The limits of error given in the original data are often ambiguous, but it is believed that the limits represent a confidence level between 65% and 95%.

Table 6. Comparison of dielectric constants of carbon dioxide at 20°C and 1 atmosphere pressure.

Reference	Year	Frequency	$(\epsilon-1) \cdot 10^6$	Limits	Ref.no.
<i>Watson and Ramaswamy</i>	1936	<i>Optical</i>	815,9	$\pm 0,5$	83
<i>Cuthbertson and Cuthbertson</i>	1920	<i>Optical</i>	820,9	$\pm 0,7$	84
Birnbaum et al.	1951	9,28 GHz	918,3	$\pm 6,9$	85
Lyons et al.	1948	9,00 GHz	919,2	± 2	86
Watson et al.	1931	1 MHz	919,4	± 2	87
Lovering and Wiltshire	1951	100 kHz	919,7	± 2	49
Zieman	1952	9,47 GHz	920,1	$\pm 4,1$	88
Hector and Woernley	1946	1 MHz	920,1	± 2	89
Jasinski and Berry	1954	3,36 GHz	920,57	$\pm 0,7$	90
Essen and Froome	1951	24 GHz	<u>920,78</u>	± 2	91
Watson	1934	1 MHz	<u>921,5</u>	± 1	33
Dunn	1964	1,6 kHz	921,62	$\pm 0,3$	69
Bergström (this thesis)	1973	10 kHz	922,2	$\pm 0,3$	-
Birnbaum	1951	MW	<u>922,4</u>	-	77
NBS recommended value	1953	-	922	± 1	77

Table 7. Comparison of dielectric constants of hydrogen at 20°C and 1 atmosphere pressure.

Reference	Year	Frequency	$(\epsilon-1) \cdot 10^6$	Limits	Ref.no
<i>Lovering and Wiltshire</i>	1951	100 kHz	251,6	$\pm 1,4$	49
Essen	1953	9,2GHz	<u>253,4</u>	$\pm 0,4$	92
Hector and Woernley	1946	1 MHz	253,4	± 1	89
Koch	1913	Optical	<u>253,6</u>	$\pm 0,4$	93
Kirn	1921	Optical	<u>253,7</u>	$\pm 0,1$	94
Bergström (this thesis)	1973	10 kHz	253,8	$\pm 0,3$	-
Watson	1931	1 MHz	254,0	± 1	87
Cuthbertson and Cuthbertson	1910	Optical	<u>254,1</u>	$\pm 0,2$	95
Tausz and Görlachter	1931	Optical	<u>254,3</u>	$\pm 0,4$	96
NBS recommended value	1953	-	253,8	$\pm 0,3$	77

Table 8. Comparison of dielectric constants of nitrogen at 20°C and 1 atmosphere pressure.

Reference	Year	Frequency	$(\epsilon-1) \cdot 10^6$	Limits	Ref.no
<i>Lovering and Wiltshire</i>	1951	100 kHz	538,6	$\pm 1,4$	49
<i>Hector and Woernley</i>	1946	1 MHz	540,0	± 1	50
Lyons et al.	1948	9,00 GHz	546,9	± 2	86
Birnbaum et al.	1951	9,28 GHz	546,9	$\pm 4,1$	85
Zieman	1952	9,47 GHz	547,0	± 2	88
Watson	1934	1 MHz	547,2	± 1	33
Tausz and Görlachter	1931	Optical	<u>547,24</u>	$\pm 0,4$	96
Birnbaum	1951	MW	<u>547,3</u>	-	77
Bergström (this thesis)	1973	10 kHz	547,3	$\pm 0,3$	-
Dunn	1964	1,6 kHz	547,40	$\pm 0,2$	69
Watson and Ramaswamy	1936	Optical	547,9	$\pm 0,4$	83
Essen and Froome	1951	24 GHz	<u>548,07</u>	$\pm 0,2$	91
Essen	1953	9 GHz	<u>548,07</u>	$\pm 0,2$	92
Koch	1913	Optical	<u>548,25</u>	$\pm 0,4$	98
Jasinski and Berry	1954	3,36 GHz	548,74	$\pm 0,4$	90
Cuthbertson and Cuthbertson	1909	Optical	<u>548,9</u>	$\pm 0,4$	95
NBS recommended value	1953	-	548,0	$\pm 0,5$	77

The values recommended by NBS are based on the underlined values. The principal emphasis has been placed on the optical data. The microwave values have also been considered reliable. The values obtained at radio frequencies have been classed as unreliable, and are not included in the recommended values with the exception of the RF value for carbon dioxide determined by Watson³³.

Some references have been listed in italics which signifies that their data deviate from the mean of the other data by more than five times the standard deviation assumed for their results.

If the values in this work are compared with the NBS recommended values a very good agreement can be noted in the case of carbon dioxide and hydrogen. The nitrogen value, and also that of argon, is slightly outside the NBS limits.

A comparison with the values determined by Dunn⁶⁹ shows an even better agreement, i.e. within $0,1 \cdot 10^{-6}$. The carbon dioxide values, however, differ as much as $0,6 \cdot 10^{-6}$ which is probably due to the lower purity of the carbon dioxide used by Dunn. With this exception, more confidence is placed on the modern, high-precision values given by Dunn than the older recommendations from NBS.

These comparisons clearly demonstrate that the capacitance meter is working satisfactorily and is capable of producing very accurate results.

7.3. Performance tests at elevated temperatures

The capacitance meter is primarily designed for the determination of dipole moments with the temperature variation method. This method is based on Debye's equation (3) which is repeated here for the convenience of the reader.

$$P_M = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (3)$$

In order to evaluate the dipole moment, μ , the dielectric constant, ϵ , and the gas density, ρ , have to be determined at different temperatures.

To test the precision of the results when the measuring capacitors were operated at elevated temperatures, a series of measurements of the dielectric constant of nitrogen was performed at 35°C, 45°C and 55°C. The results at 35°C and 45°C are tabulated below in table 9. At 55°C the readings were unstable. This was at least partly due to poor thermostating. However, a few measurements were carried out at 55°C, but the results were too scattered to be useful in this context. It was thus decided not to exceed 45°C in the dipole moment determinations.

Table 9. Dielectric constant of nitrogen measured at 35°C and 45°C.

35°C. $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}} \cdot 10^6$		45°C. $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}} \cdot 10^6$	
547,39	$\bar{x} = 547,34$	547,23	$\bar{x} = 547,35$
547,30	$s_x = 0,06$	547,41	$s_x = 0,08$
547,38	$s_{\bar{x}} = 0,03$	547,36	$s_{\bar{x}} = 0,04$
547,26		547,44	
547,38		547,33	

It is evident from table 5 and 9 that there is no statistically significant difference between the dielectric constants measured at 25°C, 35°C and 45°C.

7.4. Gas density measurements

The gas density required by Debye's equation for the evaluation of the dipole moment has nearly always been determined by pressure measurements. Such determinations below a pressure of 10 mmHg are not so easily done with accuracy. For this reason another approach was tried in this work. If the volume of the measuring cell is known, the substance to be investigated can be weighed in an ampoule with high accuracy. In this way a good measure of the gas density is obtained, assuming a negligible adsorption of the gas on the walls of the measuring cell. To suit this technique the Clausius-Mossotti expression for the molar polarization (1) is rewritten as

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M \cdot V}{m} \quad (42)$$

where m is the weight of the substance in an ampoule and V is the volume of the measuring cell.

In order to assess the volume of the measuring cell with sufficient accuracy the cell was weighed with water several times. The filling of the cell was done in vacuo to facilitate the filling and for degassing the water. The weighings were performed at 25°C and 45°C. The volume was found to be $191,27 \pm 0,05 \text{ cm}^3$ at 25,0°C and $191,42 \pm 0,05 \text{ cm}^3$ at 45,0°C.

Small capillary glass tubes about five centimeters long were used as ampoules. By close control of the inner diameter of the capillary tube, the amount of substance could be approximately controlled by a simple length measurement at the filling procedure. When filling the preweighed empty ampoules special precautions were taken as to exclude moisture from the air. After the ampoules had been sealed they were weighed again on a Sartorius 4125 electrodynamic balance, using matched capillary tubes as counterweights, thus ensuring a high accuracy in the weight. The amount of substance in each ampoule

was about one milligram, with the exception of acetone. In this case about 10 milligrams were filled in each ampoule and the weighings were made on a conventional Mettler semi-micro balance. All weighings were reduced to mass.

7.5. Tests of ampoule technique

To test the performance of this ampoule technique, used instead of the conventional pressure determinations, it was decided to determine the dipole moment of acetone, which is the only ketone having a fairly well determined dipole moment in the gas phase⁹⁹.

7.5.1. Purity of acetone sample.

Acetone used in this test was a commercial sample from The British Drug Houses Ltd. The 'Aristar' quality used, is controlled by g.l.c. measurements by the manufacturer and should not contain impurities. However, an additional check was done with a Varian 600 D analytical gas chromatograph with a column of Chromosorb W with 10% Carbowax 20 M as the stationary phase. No impurity could be detected.

The water content of the acetone sample was determined by gas chromatography using a Porapak Q column¹⁰⁰ in a Varian 90 P gas chromatograph. Benzene, saturated with water, was used as a water standard.

The acetone sample was repeatedly dried with Molecular Sieve type 4A, (8-12 mesh). The water content was then measured and found to be 5 p.p.m. This is a more than satisfactory low water content since several hundred parts per million could have been tolerated.

7.5.2. Experimental technique

The procedure for determining the dielectric constant of acetone vapour is very similar to the technique used for the non-polar gases. However, dry nitrogen of atmospheric pressure first has to be admitted to permit loading an acetone ampoule in the ampoule chamber. After having replaced the indium O-ring seal with a new one, the cell was evacuated. This operation necessitated the removal of the cell assembly from the thermostat and was preferably done in the evening, so that the assembly could come to thermal equilibrium overnight. Then the capacitance of the evacuated capacitor was determined, the acetone ampoule was broken and when the acetone vapour had come to thermal equilibrium new readings were taken.

Several determinations were made with empty ampoules to check for possible discontinuities when the electromagnetically operated ampoule breaker was actuated. However, not the slightest change in capacitance could be detected in these tests. Frequent tests were also made with nitrogen for periodical controls of the performance of the apparatus.

7.5.3. Molar polarization of acetone

Determinations of the dielectric constants for acetone in the gas phase were made at 25, 35 and 45°C. The measurements were made in the pressure interval of 15 - 35 mmHg, with a majority of measurements carried out at about 20 mmHg. The resulting molar polarizations are shown in table 10.

Table 10. Molar polarizations of acetone vapour.

T = 298,18 K	T = 308,13 K	T = 318,21 K
187,45	181,92	176,24
187,26	182,27	176,56
187,33	181,68	176,73
187,04	181,80	176,92
187,58	182,07	176,94
187,21	181,83	177,13
187,37	181,93	176,86
187,56		176,64
187,13		176,58
187,43		176,68
187,12		
187,23		
187,34		
187,24		
187,62		
187,67		

The molar polarizations are summarized in table 11. The uncertainties

Table 11. Summary of molar polarization for acetone in the gas phase.

T K	$P_M \text{ cm}^3 \cdot \text{mol}^{-1}$	No. of detns.	Pressure interval, mmHg
298,18	$187,35 \pm 0,09$	16	14 - 37
308,13	$181,93 \pm 0,15$	7	13 - 27
318,21	$176,73 \pm 0,16$	10	14 - 30

for the molar polarizations are twice the standard error of the mean.

7.5.4. Adsorption test.

To check any possible dependence of the molar polarization, P_M , on the gas density, a plot of molar polarizations versus the sample weights, m , was drawn at three temperatures (see figure 30). With the least squares method three lines were fitted. To test if the three lines could be considered to be horizontal 90 percent confidence intervals were calculated for the slopes of the lines. This test was made to detect a possible adsorption causing a decrease of the gas density. The result is given in table 12.

Table 12. Slope of the molar polarization as a function of the sample weight.

Temp. °C	Slope with conf.interval, $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{mg}^{-1}$	Number of data points
25	$-0,00050 \pm 0,028$	16
35	$-0,015 \pm 0,052$	7
45	$+0,0033 \pm 0,053$	10

Since the confidence intervals well include zero the slopes are to be considered horizontal. The small deviations from zero are probably due to statistical variations since a larger number of data points results in a smaller deviation from zero.

7.5.5. Dipole moment of acetone

By fitting the data in table 10 with the method of least squares to Debye's equation (3), see figure 31, the following expression is



Figure 30. Molar polarization of acetone as a function of sample weight.

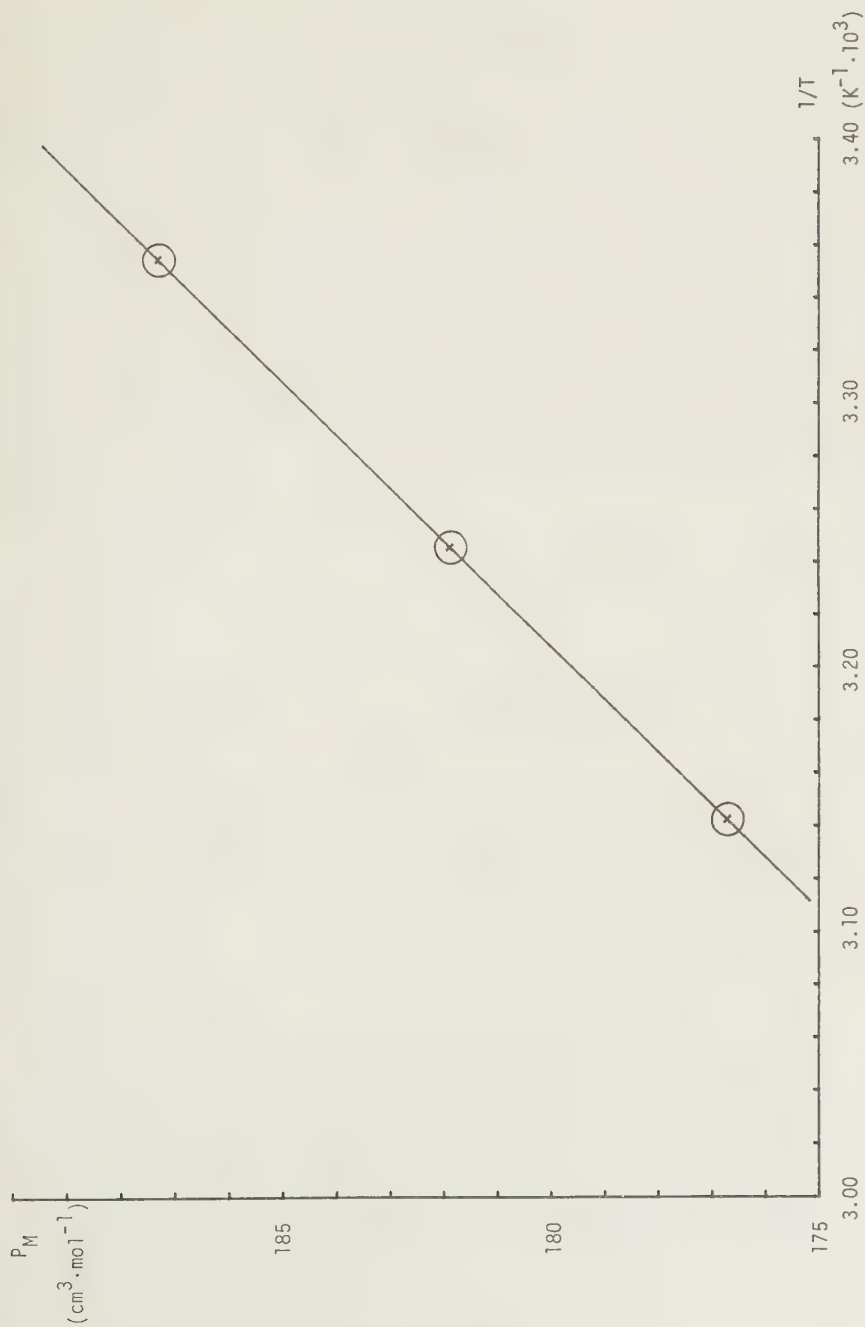


Figure 31. Molar polarization of acetone as a function of the inverse absolute temperature.

obtained:

$$P_M = 18,7 + 50296 \cdot \frac{1}{T} \quad (43)$$

The deformation polarization, P_D , i.e. the sum of the electronic and atomic polarizations, is rather unreliable due to the small temperature interval used. Applying a 90 percent confidence interval the deformation polarization is $P_D = 18,7 \pm 2,2 \text{ cm}^3 \text{ mol}^{-1}$. The same confidence interval for the slope, B , of the Debye plot is $B = 50296 \pm 393 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. The dipole moment can thus be calculated from the Debye equation (3) as

$$\mu^2 = \frac{9k}{4\pi N} \cdot B \quad (44)$$

or

$$\mu = 0,0128130\sqrt{B} \quad (45)$$

The dipole moment for acetone in the gas phase between 25 and 45°C was determined to $\mu = 2,87 \pm 0,01 \text{ D}$. The limits given are statistical 90 percent confidence limits.

7.5.6. Comparison of results.

In table 13 the determination is compared with other data and especially with the selected value compiled by NBS⁹⁹. The present value of the dipole moment, 2,87 D, is in good agreement with the NBS selected value, 2,88 D. A good agreement can also be noted with the three values 2,87, 2,88 and 2,89 D obtained by the same method, designated DT. The values obtained by microwave spectroscopy tend to be slightly

Table 13. Comparison of dipole moments of acetone in the gas phase.

Reference	Year	Method	Temp.(°C)	Moment(D)	Limits	Ref.no.
Stuart	1928	DT	20-180	2,87	$\pm 0,04$	27
Bergström (this thesis)	1973	DT	25-45	2,87	$\pm 0,01$	-
Zahn	1932	DR	30-180	2,88	-	104
Boggs, Crain, and Whiteford	1957	DT ^a	30-90	2,88	$\pm 0,01$	43
Buckingham and Le Fèvre	1953	DT	85-315	2,89	$\pm 0,02$	102
Swalen and Costain	1959	MW	-	2,90	-	101
Peter and Dreizler	1964	MW	-	2,93	$\pm 0,03$	105
Ramaswamy	1936	DR	23-95	2,95	-	103
Höjendahl ^b	1928	DR	100	2,97	-	106
NBS selected value	1967	-	-	2,88	$\pm 0,03$	99

The method code is MW=microwave spectroscopy, DT = dielectric constant as a function of temperature, and DR = dielectric constant and refractive index data.

^a Microwave frequency.

^b Calculation from dielectric constant values by Pohrt¹⁰⁸.

higher. Table 13 also shows the temperature intervals used, which are three to twelve times larger than in this work.

It can be concluded that the ampoule technique works satisfactorily at least in the pressure range 10 to 50 mmHg.

8. DIPOLE MOMENTS OF KETONES IN THE GAS PHASE

It was originally intended to make a systematic investigation of both straight-chain and branched ketones up to hexanones, since, with one exception¹⁰⁷, the dipole moment in the gas phase has not been determined for aliphatic ketones other than acetone. However, the original plan was modified since it could be expected that the dipole moment should roughly remain constant as long as methyl groups in the α -positions do not make the ketone molecule sterically hindered. Thermochemical results show that 2,2,4,4-tetramethyl-3-pentanone seems to be sterically hindered but not 2,2,4-trimethyl-3-pentanone¹⁰⁹. A steric hindrance should increase the C-C-C angle at the carbonyl group, thus decreasing the dipole moment. Consequently it would be very interesting to determine the dipole moments of these two ketones.

8.1. Vapour pressures of 2,2,4 - trimethyl - 3 - pentanone and 2,2,4,4 - tetramethyl - 3 - pentanone.

It is not desirable to make measurements at too high pressures of a substance due to the possibility of partial condensation^{49,110}. The vapour pressure at 25°C of e.g. 2,2,4 - trimethyl-3-pentanone can be calculated from vapour pressure data¹¹¹ to be 2,2 mmHg. The boiling point of 2,2,4,4 - tetramethyl - 3 - pentanone is about 15°C higher than that of 2,2,4 - trimethyl - 3 - pentanone so the maximum measuring pressure should not be much over 1 mmHg for these two ketones. This low pressure imposes severe demands on the apparatus. The measuring capacitance should have been much larger for a case like this. However, it was thought feasible to carry out the measurement of the dipole moment for the two ketones, although accuracy would be expected to be impaired.

8.2. Experimental procedure and dipole moment of 2,2,4 - trimethyl - 3 - pentanone.

Determinations of the dielectric constant of 2,2,4 - trimethyl - 3 - pentanone were made at 25, 35 and 45°C. The measurements were performed in the pressure interval of 0,9 - 1,5 mmHg.

Purified 2,2,4 - trimethyl - 3 - pentanone was kindly supplied by Dr Peter Sellers, Thermochemistry Laboratory, Chemical Center, Lund. The purification method has been described elsewhere¹⁰⁹. The 2,2,4 - trimethyl - 3 - pentanone was repeatedly dried with Molecular Sieve as described for acetone. The water content was about 30 p.p.m.

The dielectric constant measurements did show that partial condensation took place at pressures over 1,5 mmHg at 25 and 35°C.

A plot of the dielectric constant against the sample weight was made for the three temperatures used. The fact that the extrapolated lines did not pass the origin of the coordinates indicated that a small amount of the ketone was adsorbed on the walls in the measuring cell. However, this amount could be found as the intersections of the extrapolated lines and the sample weight axis (i.e. $\epsilon - 1 = 0$), for the reason that the amount of adsorbed ketone seemed to be constant in the investigated pressure interval. In this way weight corrections for different temperatures could be applied to give the true gas density.

To check this procedure, a few pressure measurements were made in order to get a second, independent determination of the gas density. The pressure measurements were made with a capacitive differential pressure meter, Rosemount Engineering Co., type 831A2, calibrated against known vapour pressures. The results were in very good agreement with those obtained by weight correction.

18 individual molar polarizations so obtained can be found in table 14 and a summary in table 15. The spread given for the molar polarizations in table 15 is twice the standard error of the mean.

Table 14. Molar polarizations of 2,2,4 - trimethyl - 3 - pentanone in the gas phase.

T = 298,21 K	T = 308,14 K	T = 318,21 K
180,89	174,98	170,20
180,47	174,70	169,54
180,56	174,79	170,22
180,03	174,68	169,50
179,49	174,87	170,51
180,56	175,45	169,07

Table 15. Summary of molar polarizations of 2,2,4 - trimethyl - 3 - pentanone in the gas phase.

T K	$P_M \text{ cm}^3 \cdot \text{mol}^{-1}$	No. of detns.	Pressure range, mmHg
298,21	$180,33 \pm 0,40$	6	0,95 - 1,25
308,14	$174,91 \pm 0,25$	6	1,05 - 1,30
318,21	$169,84 \pm 0,45$	6	1,15 - 1,45

From the data in table 14 the following equation is obtained by the method of least squares:

$$p_M = 13 + 49791 \cdot \frac{1}{T} \quad (46)$$

As a result of the larger uncertainty in the measured molar polarizations as compared to that of acetone, the deformation polarization has an exceedingly large confidence interval (90%) : $P_D = 13 \pm 8 \text{ cm}^3 \cdot \text{mol}^{-1}$. The same confidence limits applied to the slope give $B = 49791 \pm 2130 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ which results in a dipole moment of $\mu = 2,86 \pm 0,06 \text{ D}$ for 2,2,4-trimethyl-3-pentanone in the gas phase.

Since the only values of the dipole moments of ketones in the gas phase to be found in the literature are those of acetone in table 13 and a single value of 2-butanone¹⁰⁷, no comparison can be made with literature values. The value of the dipole moment will be discussed later.

8.3. Experimental procedure and dipole moment of 2,2,4,4 - tetramethyl - 3 - pentanone

The dielectric constants of 2,2,4,4 - tetramethyl - 3 - pentanone in the gas phase were measured at 25, 35 and 45°C. The pressure range used in the measurements was approximately the same as for 2,2,4 - trimethyl - 3 - pentanone, i.e. 0,5 - 1,4 mmHg.

A commercial purum grade sample of 2,2,4,4 - tetramethyl - 3 - pentanone (Fluka AG) was purified by preparative gas chromatography. This was done using a Perkin-Elmer F-21, equipped with a flame ionization detector and a column of Chromosorb W with 20% Carbowax 20 M as the stationary phase. Eleven compounds were present as distinguishable impurities in the original sample. They were removed with one exception. When this impurity concentration had been reduced to

150 p.p.m. as estimated from the chromatogram, this value was regarded as satisfactory. The ketone was dried with Molecular Sieve and the water content was determined to 30 p.p.m.

A plot of the dielectric constant versus the sample weight was made for the three temperatures used. As in the case of 2,2,4 - trimethyl - 3 - pentanone the extrapolated lines did not pass the origin of the coordinates, indicating adsorption on the cell walls. In this case the values obtained from the intersections of the extrapolated lines and the sample weight axis could not be used for correction purposes as there were indications that the amount of adsorbed ketone could not be considered constant in the pressure range used for measurements. In order to determine the adsorbed amounts of ketone and the pressure dependence, four pressure measurements were made at each temperature. From these pressure determinations accurate adsorption corrections could be calculated and then subtracted from the weighings to give the real gas density.

The molar polarizations calculated from 24 determinations of the dielectric constant and the gas density are shown in table 16. In table 17 the molar polarizations are summed up and presented with limits derived as twice the standard error of the mean.

Table 16. Molar polarizations of 2,2,4,4 - tetramethyl - 3 - pentanone in the gas phase.

T = 298,21 K	T = 308,15 K	T = 318,22 K
167,23	162,31	157,16
167,51	163,54	157,58
167,68	162,94	157,68
166,93	162,54	158,41
166,88	162,22	159,58
167,94	161,87	159,47
166,21	163,03	157,30
167,86		157,82
167,20		

Table 17. Summary of molar polarizations of 2,2,4,4 - tetramethyl -
- 3 - pentanone in the gas phase.

T K	$P_M \text{ cm}^3 \cdot \text{mol}^{-1}$	No.of detns.	Pressure range, mmHg
298,21	$167,27 \pm 0,35$	9	0,50 - 1,20
308,15	$162,64 \pm 0,40$	7	0,70 - 1,10
318,22	$158,12 \pm 0,65$	8	0,75 - 1,35

From the molar polarizations and absolute temperatures given in table 16 the following expression is obtained by the method of least squares:

$$P_M = 22 + 43362 \cdot \frac{1}{T} \quad (47)$$

The uncertainty in deformation polarization, slope, and dipole moment is slightly larger than that of 2,2,4 - trimethyl - 3 - pentanone, mainly due to a wider scattering of the molar polarization results at 45°C. The slope is $B = 43362 \pm 2730 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ given with a 90 percent confidence interval. The dipole moment of 2,2,4,4 - tetramethyl - 3 - pentanone in the gas phase is consequently $2,67 \pm 0,08 \text{ D}$.

8.4. Comparison of results with benzene solution measurements.

It has been mentioned before that reliable dipole moment data for aliphatic ketones in the gas phase is lacking with the exception of acetone. A comparison with dipole moments measured in solution is not particularly fruitful in this case for three reasons. Firstly, the interaction between solute and solvent alters the dipole moment in a way that only partly can be predicted. This has already been pointed out in section 3. Secondly, the dipole moment values obtained in solution are often not very accurate and thirdly, no dipole moment of 2,2,4 - trimethyl - 3 - pentanone could be found in the literature.

If, in spite of this, a comparison is made with dipole moments determined in solution, the solvent should be benzene. Generally speaking, benzene seems to be the most inert solvent which is illustrated in table 1. A collection of dipole moments for aliphatic ketones measured in benzene can be found in table 18. Most values have been compiled by McClellan²⁶.

Table 18. Compilation of dipole moments for aliphatic ketones measured in benzene solution. (The figures in brackets are the number of data from which the mean has been calculated.)

a) Straight-chain ketones.

2 - propanone 2,78 D (11)

2 - butanone 2,78 D (5)

2 - pentanone 2,74 D (3) 3 - pentanone 2,73 D (2)

2 - hexanone 2,72 D (2)

2 - heptanone 2,61 D (1) 3 - heptanone 2,81 D (1) 4-heptanone
2,71 D (2)

2 - octanone 2,72 D (1)

b) Branched ketones.

3 - methyl - 2 - butanone	2,77 D (2)
2,2 - dimethyl - 3 - butanone	2,81 D (1)
2,4 - dimethyl - 3 - pentanone	2,73 D (2)
2,2,4,4 - tetramethyl - 3 - pentanone	2,79 D (1)

It is evident from tables 13 and 18 that the dipole moment is lower in benzene solution than in the gas phase by approximately 0,1 D. This fact has been empirically formulated by e.g. Le Fèvre and coworkers¹⁰² and more recently Cumper and Langley¹¹³. It can also be seen that the dipole moment is approximately constant (within the experimental uncertainty) irrespective of chain length and whether the ketone is branched or not. This constancy is especially apparent in a recent series of Cumper and Langley¹¹³ giving 2,78, 2,79, 2,77 D for 2 - propanone, 2 - butanone and 2 - pentanone respectively.

A constant dipole moment in the gas phase has also been found in this work with the values $2,87 \pm 0,01$ D of acetone and $2,86 \pm 0,06$ D of 2,2,4 - trimethyl - 3 - pentanone.

The value of 2,79 D of 2,2,4,4 - tetramethyl - 3 - pentanone measured by Wolf¹¹⁴ in 1929 also seems to be the same as for the other ketones. A second value of $2,48 \pm 0,02$ D can be found in the literature. This very low value has been published by Cherrier¹¹⁵, but unfortunately the solvent is not stated. Judging from a previous work¹¹⁶ of his, it seems probable that benzene has been used as solvent.

A direct comparison with the present gas phase dipole moment of $2,67 \pm 0,08$ D and the value of Cherrier, $2,48 \pm 0,02$ D with 0,1 D added is treacherous and should not be made. However, his value

might be an indication that the dipole moment of this sterically hindered ketone molecule is indeed lower than the dipole moments of non-hindered ketones.

8.5. Correlation between dipole moment and C-C-C bond angle at the carbonyl group.

A possible correlation between the C-C-C angle at the carbonyl group and the dipole moment (gas phase) of a ketone can not be based solely on aliphatic ketones because of paucity of data. Table 19 gives a compilation of angles and dipole moments for aliphatic and alicyclic ketones determined by microwave spectroscopy.

Table 19. Dipole moments and C-C-C angles at the carbonyl group for aliphatic and alicyclic ketones.

Compound	Dipole moment, (D)	Angle	Reference
Acetone	2,90	$116^{\circ}7'$	101
Acetone	$2,93 \pm 0,03$	$120,32^{\circ}$	105
<i>trans</i> -2-butanone	$2,775 \pm 0,015$	$117^{\circ}12'$	107
Cyclopropanone	$2,67 \pm 0,10$		117
Cyclopropanone		$64^{\circ}36' \pm 50'$	118
Cyclobutanone	$2,89 \pm 0,03$	$93,1^{\circ} \pm 0,3^{\circ}$	119
Cyclopentanone	$3,25 \pm 0,02$	$110,5^{\circ} \pm 0,7^{\circ}$	120
Cyclopentanone		109°	121
Cyclohexanone	$2,87 \pm 0,04$	$117^{\circ} \pm 3^{\circ}$	122
Bicyclo[2.1.1]hexane-2-one	$3,35 \pm 0,02$		123
Bicyclo[2.1.1]hexane-5-one	$3,18 \pm 0,02$		124

The dipole moment of *trans*-2-butanone seems to be remarkably low. In fact, it is the same value as obtained in benzene solution (see table 18). The gas phase value should be expected to be nearly the same as that of acetone since the angle at the carbonyl group is almost the same in 2-butanone as in acetone.

The two isomeric bicyclohexanones listed in table 19 have interestingly high values of the dipole moment but unfortunately it has not been possible to locate values of their angles in the literature.

Thus only five ketones remain to be plotted in figure 32.

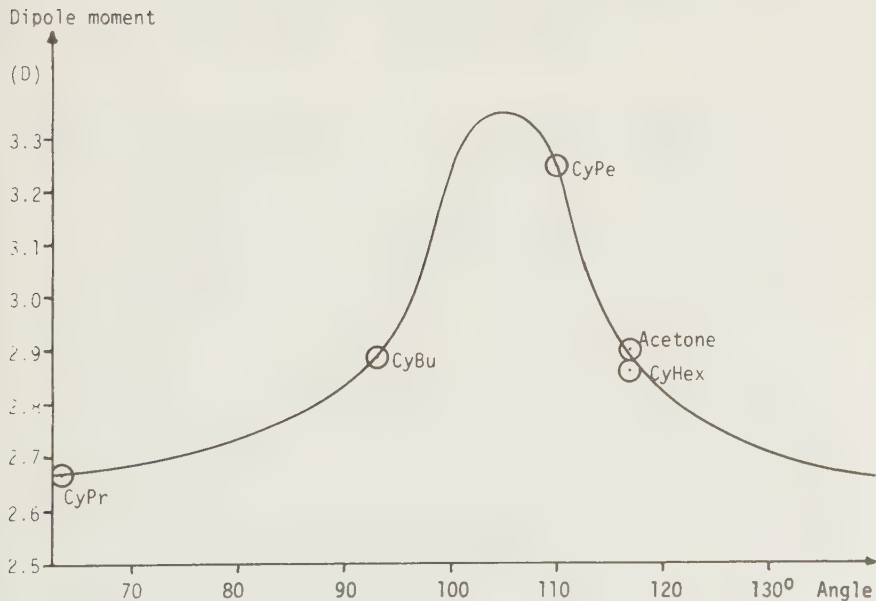


Figure 32. Plot of dipole moment versus the C-C-C angle at the carbonyl group for some ketones. (Microwave spectroscopy data from table 19.)

A relationship between dipole moment and the C-C-C angle at the carbonyl group is shown in figure 32. A smooth curve connecting the five points will be approximately bell-shaped.

If the curve is used for estimating an angle from a dipole moment value, the estimate will be very rough because the curve is not well determined. Especially above 120° the extrapolation is extremely uncertain.

A dipole moment value of 2,67 D as for 2,2,4,4 - tetramethyl - 3 - pentanone will thus correspond to an angle in the vicinity of 140° .

ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor Stig Sunner for initiating this work as well as for his support and positive criticism throughout the course of the work.

I am greatly indebted to Professor Lennart Stigmark who kindly put laboratory facilities at my disposal. His encouraging advice during the years has also been invaluable. The transformer bridge in this work is based on an earlier construction made by him.

It is a pleasure to thank Professor Bertram Broberg for a valuable discussion on the pressure dependence of the capacitance. The assistance of Dr. Magnus Koch, Inst. for Electrical Measurements, Chalmers Univ. of Techn., Gothenburg with the first capacitance calibration is gratefully acknowledged.

I am very grateful to Mr. Alf Lundberg for his patience with the most crucial part of the work, the glass capacitors, and for many other glass details, to fil. lic. Lars-Gunnar Torstensson, Dept. of Analytical Chemistry, for his most valuable help with many weighings, to Dr. Peter Sellers for a ketone sample and for linguistic criticism, and to Miss Monica Andersson for all important g.l.c. determinations.

I am also indebted to ing. Ingvar Jonsson for many helpful discussions on the electronic circuitry. The laboratory work done by my wife, Stina, and Mr. Tore Henriksson has been of great help. Messrs. Börje Pettersson, Jan-Erik Falk, and Jan-Erik Lindahl in the Chemical Center workshop did the mechanical construction and their work is much appreciated. My thanks are also due to Messrs. Per-Olof Agren, Lars Hedenstjerna, and Bo Nilsson who helped with many mechanical devices and to Miss Ulla-Britt Gavelin who did the efficient typing of the manuscript.

To all friends and colleagues who have helped in many different ways I extend my appreciation.

Appendix 1

The derivation of the expression used for converting the $(\epsilon-1)_{t,0,p \text{ atm}}$ data to $(\epsilon-1)_{20^\circ\text{C}, 1 \text{ atm}}$ is very straightforward and has first been made by Dunn⁶⁹. It includes the combination of the Clausius-Mosotti equation (1),

$$P_M = \frac{(\epsilon-1) \cdot M}{(\epsilon+2) \cdot \rho} = \frac{4\pi}{3} \alpha N \quad (1)$$

giving the relation between the molar polarization, P_M , the dielectric constant, ϵ , the molecular weight, M , and the gas density, ρ , and Berthelot's equation of state

$$pV = nRT \left[1 + \frac{9}{128} \cdot \frac{T_C}{p_C} \cdot \frac{p}{T} \left(1 - \frac{6T_C^2}{T^2} \right) \right] \quad (41a)$$

Equation (1) can be written

$$\frac{\epsilon-1}{(\epsilon+2)P_M} = \frac{n}{V} \quad (41b)$$

If (41a) and (41b) are combined the result will be

$$(\epsilon-1)_{t,p} = (\epsilon+2)P_M \cdot \frac{p}{RT} \left[1 + \frac{9}{128} \cdot \frac{T_C}{p_C} \cdot \frac{p}{T} \left(1 - \frac{6T_C^2}{T^2} \right) \right]^{-1} \quad (41c)$$

and

$$\begin{aligned}
 (\epsilon-1)_{20^{\circ}\text{C}, 1 \text{ atm}} &= (\epsilon+2)P_M \cdot \frac{1(\text{atm})}{R \cdot 293,16} \cdot \\
 &\cdot \left[1 + \frac{9}{128} \cdot \frac{T_C}{P_C} \cdot \frac{1(\text{atm})}{293,16} \left(1 - \frac{6T_C^2}{293,16^2} \right) \right]^{-1} \quad (41d)
 \end{aligned}$$

Since the variation of $(\epsilon+2)$ with temperature and pressure is negligible we have

$$\begin{aligned}
 \frac{(\epsilon-1)_{t,p}}{(\epsilon-1)_{20^{\circ}\text{C}, 1 \text{ atm}}} &= \frac{p}{1(\text{atm})} \cdot \frac{293,16}{T} \cdot \\
 &\cdot \frac{\left[1 + \frac{9}{128} \cdot \frac{T_C}{P_C} \cdot \frac{1(\text{atm})}{293,16} \left(1 - \frac{6T_C^2}{293,16^2} \right) \right]}{\left[1 + \frac{9}{128} \cdot \frac{T_C}{P_C} \cdot \frac{p}{T} \left(1 - \frac{6T_C^2}{T^2} \right) \right]} \quad (41)
 \end{aligned}$$

References.

1. Faraday, M., Experimental Researches in Electricity, Vol.I, B. Quaritch, London (1839).
2. Mosotti, O.F., Mem. di Mathem. e di Fisica in Modena, 24, II, 49 (1850).
3. Clausius, R, Mechanische Wärmetheorie, Bd.2, Vieweg, Braunschweig 1879, p.62.
4. Debye, P., Phys. Z., 13, 97 (1912).
5. Debye, P., Verh. dtsch. phys. Ges., 15, 777 (1913).
6. Debye, P., Polar Molecules, Chemical Catalog Co., New York 1929.
7. Langevin, P., J. phys., (4) 4, 678 (1905).
8. Langevin, P., Ann. chim. phys., (8) 5, 70 (1905)
9. Onsager, L., J. Am. Chem. Soc., 58, 1486 (1936).
10. Van Vleck, J.H., Phys. Rev., 29 727 (1927).
11. Van Vleck, J.H., Phys. Rev., 30 31 (1927).
12. Van Vleck, J.H., The Theory of Electric and Magnetic Susceptibilities, Oxford, London 1932, chap. VII.
13. McClellan, A.L., Tables of Experimental Dipole Moments, Freeman, San Francisco 1963, p.2.
14. Gerlach, W. and Stern, O., Ann. der Physik, 74 673 (1924).
15. Estermann, I. and Fraser, R.G.J., J. Chem. Phys., 1 391 (1933).
16. Rabi, I.I., Zacharias, J.R., Millman, S., and Kusch, P., Phys. Rev., 53 318 (1938).
17. Cleeton, C.E. and Williams, N.H., Phys. Rev. 45 234 (1934).
18. Gilliam, O.R., Johnson, C.M. and Gordy, W., Phys. Rev., 78 140 (1950).

19. Dakin, T.W., Good, W.E., and Coles, D.K., Phys. Rev., 70 560 (1946).
20. Hughes, R.H., and Wilson, E.B., Phys. Rev., 71 562 (1947).
21. Mc Clellan, A.L., Tables of Experimental Dipole Moments, Freeman, San Francisco 1963, p.1.
22. Lide, D.R., Jr., J. Chem. Phys., 38 2027 (1963).
23. Müller, H., Phys. Z., 34 689 (1933).
24. Müller, H., Phys. Z., 35 346 (1934).
25. Müller, H., Trans. Far. Soc., 30 731 (1934).
26. Mc Clellan, A.L., Tables of Experimental Dipole Moments, San Francisco, 1963.
27. Stuart, H.A., Z. Physik, 51 490 (1928).
28. Smyth, C.P., Dipole Moments, in Weissberger, A., ed., Physical Methods of Organic Chemistry, Interscience, New York 1960, Vol.I, Part III, Chap. 39.
29. Zahn, C.T., Phys. Rev., 24 400 (1924).
30. Stuart, H.A., Z. Physik, 47 457 (1928).
31. McAlpine, K.B. and Smyth, C.P., J. Am. Chem. Soc., 55 453 (1933).
32. Stranathan, J.D., Rev. Sci. Instr., 5 334 (1934).
33. Watson, H.E., Proc. Roy. Soc., A143 558 (1934).
34. Coop, I.E. and Sutton, L.E., J. Chem. Soc., 1269 (1938).
35. Bloom, G.I.M. and Sutton, L.E., J. Chem. Soc., 727 (1941).
36. Wiswall, R.H. and Smyth, C.P., J. Chem. Phys., 9 352 (1941).
37. Hurdis, E.C. and Smyth, C.P., J. Am. Chem. Soc., 64 2829 (1942).
38. Jelatis, J.G., Techn. Report No.VII, Lab. for insulation Res., MIT, (1947).
39. Gauss, E.J. and Gilman, T.S., Rev. Sci. Instr., 31 164 (1960).
40. Taylor, A.H., Electronics, 19 Dec.142 (1946).
41. Crain, C.M., Rev. Sci. Instr., 21 456 (1950).
42. Pound, R.V., Rev. Sci. Instr., 17 490 (1946).

43. Boggs, J.E., Crain, C.M. and Whiteford, J.E., J. Phys. Chem., 61 482 (1957).
44. Groves, L.G. and Sugden, S., J. Chem. Soc. 1094 (1934).
45. Le Fèvre, R.J.W., Dipole Moments, Methuen, London 1964, p.36.
46. Broxon, J.W., Phys. Rev., 37 1338 (1931).
47. Bünger, W., Z. Physik, 91 679 (1934).
48. Astin, A.V.P., J. Res. NBS, 21 425 (1938).
49. Lovering, W.F. and Wiltshire, L., Proc. I.E.E., 98:II 557 (1951).
50. Elsas, A., Ann. der Physik, 35 828 (1888).
51. Trowbridge, A., Phys. Rev., 20 65 (1905).
52. Blumlein, British Patent No. 323037.
53. Starr, A.T., Wireless Eng. and Exp. Wireless, 9 615 (1932).
54. Young, C.H., Bell Lab. Record, 24 433 (1946).
55. Cole, R.H. and Gross, P.M., Rev. Sci. Instr., 20 252 (1949).
56. Clark, H.A.M. and Vanderlyn, P.B., Proc. IEE, 96 365 (1949).
57. Oatley, C.W. and Yates, J.G., Proc. IEE, 101 91 (1954).
58. Thompson, A.M., Proc. IEE, B 103 704 (1956).
59. Lynch, A.C., Proc. IEE, B104 363 (1957).
60. Thompson, A.M., IRE Trans. on Instrumentation, I7 245 (1958).
 1. McGregor, M.C., Hersh, J.F., Cutkosky, R.D., Harris, F.K. and Kotter, F.R., IRE Trans. on Instrumentation, I7 253 (1958).
62. Leslie, W.H.P., Proc. IEE, B108 539 (1961).
63. Hersh, J.F., Gen. Radio Experimenter, 36 3 (1962).
64. Mungall, A.G. and Morris, D., Rev. Sci. Instr., 34 839 (1963).
65. Dunn, A.F., Can. J. Phys., 42 53 (1964).
66. Thompson, A.M. and Lampard, D.G., Nature, 177 888 (1956).
67. Lampard, D.G., Proc. IEE, C104 271 (1957).
68. Hallén, E., Elektricitetslära, Erik Hallén, Stockholm 1953, p.51.
69. Dunn, A.F., Can J. Phys., 42 1489 (1964).

70. Kanno, M., Can. J. Phys., 42 1508 (1964).
71. Johnson, J.B., Phys. Rev., 32 97 (1928).
72. Schottky, W., Ann. Physik, 57 54 (1918).
73. Moore, R.D. and Chaykowsky, O.C., Modern Signal Processing Technique for Optimal Signal to Noise Ratios, Princeton Applied Research Corp., Princeton, N.J. (1963).
74. Coor, T., J. Chem. Ed., 45 A583 (1968).
75. Dicke, R.H., Rev. Sci. Instr., 17 268 (1947).
76. Larsson, L-G.O., Mätresultat vid användning av ett nykonstruerat fasläsningsystem till optiskt pumpad atomfrekvensnormal utnyttjande ^{23}Na , thesis, Dept. of Applied Electronics, Lund Institute of Technology, Lund, Sweden (1973).
77. Maryott, A.A. and Buckley, F., Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State, NBS Circular 537, Washington, D.C. (1953).
78. Broberg, B., private communication.
79. Hodgman, C.D., editor, Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, (1963).
80. Rikets Allmänna Kartverk, Geodetiska Byrån, private communication.
81. Berthelot, D., Travaux et Mémoires de Bureau Intern. Poids et Mésures, 13 1 (1907).
82. Kudchadker, A.P., Alani, G.H., and Zwolinski, B.d., Chem. Rev. 68 659 (1968).
83. Watson, H.E. and Ramaswamy, K.L., Proc. Roy. Soc., A156 144 (1936).
84. Cuthbertson, C. and Cuthbertson, M., Proc. Roy. Soc., A97 152 (1920).
85. Birnbaum, G., Kryder, S.J., and Lyons, H., J. Appl. Phys., 22 95 (1951).
86. Lyons, H., Birnbaum, G., and Kryder, S.J., Phys. Rev., 74 1210 (1948).

87. Watson, H.E., Rao, G.G., and Ramaswamy, K.L., Proc. Roy. Soc., A132 569 (1931).
88. Ziemann, C.M., J. Appl. Phys., 23 154 (1952).
89. Hector, L.G. and Woernley, D.L., Phys. Rev., 69 101 (1946).
90. Jasinski, W. and Berry, J.A., Proc. IEE, C101 337 (1954).
91. Essen, L. and Froome, K.D., Proc. Phys. Soc., B64 862 (1951).
92. Essen, L., Proc. Phys. Soc., B66 189 (1953).
93. Koch, J., Arkiv Mat. Astron. Fysik, 8 No.20 (1912).
94. Kirn, M., Ann. Physik, 64 566 (1921).
95. Cuthbertson, C. and Cuthbertson, M., Proc. Roy. Soc., A83 151 (1910).
96. Tausz, J. and Görlacher, H., Z. tech. Physik, 12 123 (1931).
97. Cuthbertson, C. and Cuthbertson, M., Proc. Roy. Soc., A84 13 (1911).
98. Koch, J., Arkiv Mat. Astron. Fysik, 9 No.6 (1913).
99. Nelson, R.D., Jr., Lide, D.R., Jr., and Maryott, A.A., Selected Values of Electric Dipole Moments for Molecules in the Gas Phase, National Standard Reference Data Series, NBS-10, Washington (1967).
100. Hollis, O.L. and Hayes, W.V., J. Gas Chromatogr., 4 235 (1966).
101. Swalen, J.D. and Costain, C.C., J. Chem. Phys., 31 1562 (1959).
102. Buckingham, A.D. and Le Fèvre, R.J.W., J. Chem. Soc., 1953 4169 (1953).
103. Ramaswamy, K.L., Proc. Indian Acad. Sci., 4A 108 (1936).
104. Zahn, C.T., Physik. Z., 33 686 (1932).
105. Peter, R. and Dreizler, H., Z. Naturforschg., 20a 301 (1965).
106. Höjendahl, K., Studies of Dipole Moment, København (1928).
107. Pierce, L., Ken Chang, C., Hayashi, M., and Nelson, R., J. Mol. Spectry., 32 449 (1969).
108. Pohrt, G., Ann. Physik, 42 569 (1913).
109. Sellers, P., J. Chem. Thermodynamics, 2 211 (1970).

110. Ford, L.H., J. IEE, 95 (Part II) 709 (1948).
111. Stull, D.R., Ind. Eng. Chemistry, 39 517 (1947).
112. Connor, F.R., Wave Transmission, Edward Arnold Ltd. London (1972), p.101.
113. Cumper, C.W.N. and Langley, P.G., Trans. Faraday Soc., 67 35 (1971).
114. Wolf, K.L., Z. Physik. Chem., B2 39 (1929).
115. Cherrier, C., Bull. soc. chim. France, 1076 (1948).
116. Cherrier, C., Compt. rend., 225 1306 (1947).
117. Pochan, J.M., Baldwin, J.E. and Flygare, W.H., J. Am. Chem. Soc., 90 1072 (1968).
118. Pochan, J.M., Baldwin, J.E. and Flygare, W.H., J. Am. Chem. Soc., 91 1896 (1969).
119. Sharpen, L.H. and Laurie, V.W., J. Chem. Phys., 49 221 (1968).
120. Kim, H. and Gwinn, W.D., J. Chem. Phys., 51 1815 (1969).
121. Howard-Lock, H.E. and King, G.W., J. Mol. Spectr., 35 393 (1970).
122. Ohnishi, Y. and Kozima, K., Bull. Chem. Soc. Jap., 41 1323 (1968).
123. Coffey, D., Jr. and Hooker, T.E., J. Mol. Spectr., 40 158 (1971).
124. Coffey, D., Jr., J. Mol. Spectr., 42 47 (1972).

